IMPACT OF PEATLAND DRAINAGE WATERS UPON AQUATIC ECOSYSTEMS

FINAL REPORT

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PREFACE

This study is a concise, critical summary, of published and unpublished studies of the chemistry of drainage waters from mined peatlands in Canada and abroad. An effort has been made to compare the drainage waters of mined versus undisturbed peatland sites.

An ideal study would consist of complete water analyses "before and after" draining a well-characterized (botanically, geologically, hydrologically) peatland site. A "complete" water analysis would include an examination of acid-base, and redox status, analysis of major and trace metals, and major and trace nonmetals, identification of dissolved organic species, etc. Unfortunately, no such study exists.

In many of the studies cited here, mined and undisturbed peatland waters are compared, but emanate from two different mires. Despite this, some recurring observations are noted, for example, elevated N and P concentrations from mined versus undisturbed sites. Thus, potential problems associated with peat mining are identified, and recommendations for further study are presented.

Here, I assume that the reader is familiar with the various kinds of peat and peatlands, for example, Sphagnum and Carex peats, and bogs, fens, marshes, and swamps.

These and other peatland terms are described by Stanek and Worley (1983). I further assume that the reader is well acquainted with the extent and tremendous potential of the Canadian peat resource, for energy, as a chemical feedstock, in agriculture, horticulture, and forestry.

For reasons of expediency peatland genesis and classification, vegetational ecology and hydrology are not described here. Interested readers should begin with Gorham's bibliography which houses more than 1300 peatland ecology references (Gorham et al., 1985), or the various Proceedings of the Symposia of the International Peat Society, beginning with the most recent, the 7th (Dublin, Ireland, 1984).

The literature not directly applicable to the objective outlined above has been avoided. For example,

1) water chemistry of undisturbed mires (see Appendix 1, and references therein),
2) inorganic chemistry of peats (see Appendix 2, and references therein),
3) effects of undisturbed peatlands on the hydrogeochemistry of surface waters (see, for example, Ogden, 1982; Peverly, 1982; Wieder, 1982),
4) the use of peatlands for effluent disposal (see, for example, Dierberg and Brezonik, 1985; Dolan et al., 1981), and
5) nutrient losses from drained, fertilized peatlands

used for agriculture and forestry ("organic soils"), especially N and P losses (see, for example, Ahti, 1984; Kenttamies, 1984).

SUMMARY

In general, the development of peatlands for utilization (ditching, vegetation removal, dry peat mining) has the following effects on peat bog drainage waters:

1) pH and alkalinity increase, because ditching releases more alkaline basal peat pore waters and mineral soil water,
2) N and P concentrations increase, because drainage accelerates the decomposition of organic matter,
3) Al and Fe concentrations decrease, because the waters become less acidic and more oxidizing, and
4) in some cases at least, peatland drainage has resulted in Hg remobilization.

RÉSUMÉ

L'exploitation des tourbières, c'est-à-dire l'élimination de la végétation, le creusement de tranchées et l'extraction de la tourbe sèche, a généralement les effets suivants sur les eaux de drainage des tourbières oligotrophes:

1) augmentation du pH et de l'alcalinité, car le creusement de tranchées entraîne le dégagement d'eaux plus alcalines telles que l'eau de porosité de la tourbe de base et l'eau des sols minéraux,
2) augmentation des concentrations de N et de P, car le drainage accélère la décomposition des matières organiques,
3) diminution des concentrations d'Al et de Fe, car les eaux deviennent moins acides et plus oxydantes et,
4) dans certains cas au moins, remobilisation du Hg.

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1.0 INTRODUCTION

Peatlands occupy approximately 4% of the Earth's land area, and about 30% of the land area of Finland, 17% of the land area of Sweden and Ireland, and about 12% of the land area of Canada. They are waterlogged environments, and as such they are predominantly anaerobic. As a result of anaerobiosis, carbon accumulates as organic matter in various stages of disintegration. Nitrogen, sulphur and phosphorus accumulations are concomitant with that of organic carbon. In addition to these nonmetals, some metals accumulate in organic-rich, anaerobic environments: V, Ni, Cu, Zn, Cd, Hg, Pb and U are examples.

With existing technologies fuel peat utilization requires drainage of peatlands, and this results in oxidation of the organic matter. As a consequence of peat oxidation, peat constituents are also oxidized, for example, N, S and P from their organic to inorganic forms, and the metals noted above may be liberated from their organic and inorganic (e.g. sulphide) matrices. Thus, peat decomposition suggests a possible remobilization of many elements, from the peatland to receiving waters. Nitrogen and phosphorus release may result in subsequent eutrophication, sulphur release may cause acidification, metals release may produce toxicity problems, etc.

Since the recent drop in world oil prices the level of interest in Canadian fuel peat development has waned. Projects in Saskatchewan (Buffalo Narrows), Ontario (Dunn's

Valley), Quebec (Anticosti Island), New Brunswick (Bull Pasture bog), and Nova Scotia (Barrington bog) have been temporarily(?) shelved. It appears that the only peat fuel demonstration projects being carried out are in Newfoundland at High Point and St. Shott's bogs. Understandably, few environmental impact assessment studies have been performed under Canadian conditions.

Fuel peat utilization in Finland, Ireland, and the Soviet Union is ongoing. Some potential environmental impacts of peatland drainage have been identified, and the present report is a critical summary of the results of existing studies. The gaps which exist in our knowledge of drainage effects are identified, and recommendations for further research are provided. These suggestions may prove useful should the interest in Canadian fuel peat production become stimulated once again.

A general overview of the problems associated with peat harvesting and combustion are provided by Glooschenko et al. (1985). A comprehensive review of the environmental effects of peatland drainage is available from Sallantaus (1986); his report includes approximately 600 references. The report is written in Finnish, but an English summary is included. Recent Soviet literature on peatland drainage has been compiled by Mälkönen and Paavilainen (1985).

2.0 PHYSICAL CHEMISTRY OF DRAINAGE WATERS

2.1 pH, acidity and alkalinity

The terms "pH" and "acidity" are not used consistently throughout the literature. In the peatland literature "pH" is often used as a measure of acidity. For example, "acidity was measured as pH, with separate glass and calomel electrodes" (Glaser et al. 1981). Chemists sometimes do the same thing, for example, "the pH of a substance is a measure of its acidity just as a degree is a measure of temperature" (Westcott 1978).

Strictly speaking, acidity is defined as "the measure of the capacity of a water to neutralize strong base" and is determined by titrating with base (Drever, 1982). In the present study the following definitions are used:

pH - negative logarithm of hydrogen ion activity

acidity - measure of the capacity of a water to neutralize strong base

alkalinity - measure of the capacity of a water to neutralize strong acid

Largin et al. (1976) found that the pH of waters draining oligotrophic peatlands increased following drainage. In mires that had been drained for 2-15 years they found that the mean pH rose from 4.0 to 5.5. The range of pH values observed were 3.5-5.9 (undisturbed) vs. 4.0-6.6 (mined areas). The concentration of HCO_3^- increased from a mean value of 5 mg l^{-1} to a mean value of 50 mg l^{-1} (1-18 mg l^{-1} vs. 12-90 mg l^{-1}).

Clausen and Brooks (1983b) compared the waters draining a mined peatland with the mean composition of waters draining 15 undisturbed bogs. Some of their results are as follows:

	mined bog	control bogs
pH	5.6	5.6
acidity (as $CaCO_3$, mg l^{-1})	45.0	21.3
alkalinity (as $CaCO_3$, mg l^{-1})	8.6	10.1

The relatively high pH (5.6) of the control "bogs" suggest that they are transitional poor fens (pH 4.8-5.7) or intermediate fens (pH 5.2-6.4), rather than true bogs (see Appendix 1). Thus, comparing their results (mined bog vs. control bogs) with other studies is difficult. Although there is no apparent pH difference between the two, true bogs have pH values in the range 3.7-4.2; this allows the possibility that bog drainage may have resulted in a pH increase, from 3.7-4.2 in the undisturbed state, to 5.6 after draining and mining activities began. In other words, Clausen and Brooks (1983b) have not shown that the pH does not change following drainage.

The mined bog drainage waters had greater acidity, and less alkalinity, than the control sites. Accelerated decomposition of peat subsequent to drainage is expected to increase acidity of the drainage waters.

Measuring the pH of these waters is no simple task, and the presence of particulate and dissolved organic carbon are expected to cause lowering of apparent pH values (see Appendix 1). Thus, the mean pH value reported by

Clausen and Brooks (1980, 1983b) may be lower than the true pH. No details of the pH measurement procedure are provided by those authors.

The High Point bog near Bishops Falls, Newfoundland is described as a raised Sphagnum fuscum ombrotrophic bog (Government of Newfoundland, 1984). However, the reported pH values for the undisturbed sites range from 4.83 to 8.23, spanning almost 4 orders of magnitude in H^+ activity! The pH values of the disturbed (mined) areas are lower but still highly variable, ranging from 4.56-6.95. These results are difficult to interpret: the pH values suggest that the mire varies from transitional poor fen to extremely rich fen (Appendix 1).

In the text the Newfoundland report claims that the pH of the waters draining the natural area is greater than the pH of the waters draining the mined area (Government of Newfoundland 1984). It further states that "peat mining operations decrease the pH values by releasing water laden with acidic compounds from field strips". As noted above, this may be an apparent pH lowering due to increases in POC and DOC caused by drainage and mining operations. This suggestion is supported by the observed increases in alkalinity resulting from mining: undisturbed sites contained <1 to 1.5 mg l^{-1} alkalinity whereas disturbed sites ranged from 6.4-12.0 mg l^{-1} alkalinity (as $CaCO_3$). In other words, the apparent pH decrease subsequent to peatland development may be an artefact of poor pH

measurement methodologies.

In North Carolina peatlands, Gregory et al. (1984) noticed that the pH of waters draining cleared sites was slightly lower than the pH of vegetated sites, however the pH differences were slight.

In his studies of Finnish peatlands, Sallantaus (1984) found pH values in the range 3.7-4.3 for undisturbed bogs, and in the range 4.1-6.8 for waters draining mined sites. He provides two explanations of this rise in pH upon drainage

i) efficient drainage increases deep runoff through less acidic Carex peat layers, and sometimes mineral soil water may enter the ditch network, and

ii) peat mining actually consumes the most acidic (surface) peat layer.

At the fuel peat "bog" near Cotton, Minnesota, the pH values at the basin input are roughly equal to those at the basin output; these values are approximately equal to those of the control sites (Berglund et al., 1985). At undisturbed sites the pH is in the range 5.3-7.4, suggesting that the mire is an intermediate to transitional rich fen (Appendix 1).

At the St. Shotts bog in Newfoundland, the pH of drainage waters from natural sites was in the range 5.3-6.4 vs. 4.2-5.7 for the mined sites (Government of Newfoundland 1985). These data must be scrutinized as noted above for the High Point bog: pH measurement problems may be

responsible for the apparent pH lowering upon drainage.

As further evidence that peatland drainage increases the alkalinity of drainage waters, Johansson and Olofsson (1985) provide these data for the Stormyran peatland in Sweden: background (pre-mining) values are approximately 150 μ eq. l^{-1}; during clear-cutting and ditching alkalinity increases to 300 μ eq. l^{-1}; during low runoff periods after ditching has been completed (mainly mire groundwater) alkalinity reaches a maximum of 400 μ eq. l^{-1}; during mining operations the alkalinity was 300 μ eq. l^{-1}.

When peatlands are drained, the pH of the drainage waters will depend on several factors including

i) the pH of the mire surface water in the undisturbed state,

ii) the depth and spacing of the ditches,

iii) the trophic status of the basal peat layer (e.q. minerotrophic Carex peat vs. ombrotrophic Sphagnum peat), and

iv) the mineralogy of the underlying sediments.

The pH of surface waters of ombrotrophic Sphagnum bogs is approximately 4. Since most runoff occurs as lateral surface flow, bog drainage waters are acidic. In bogs underlain by minerotrophic Carex peats draining permits flow of water from these less acidic layers. If the ditches extend as far down as the underlying mineral soil, the dissolved acids will be neutralized through attack of solid (mineral) bases

$$\underset{\text{(solid base)}}{\text{mineral}} + \underset{\text{(acid)}}{H_2CO_3^*} \longrightarrow \text{cations} + \underset{\text{(dissolved salt)}}{HCO_3^-}$$

(see also Appendix 1). In all the studies reviewed here alkalinity of peatland drainage waters increases following ditching and development.

Accompanying the alkalinity increase an increase in pH is expected. In many cases this has been demonstrated (Largin et al., 1976, 1984; Sallantaus, 1984, and others). In some cases pH decreases have been observed (Government of Newfoundland, 1984, 1985). Although these pH decreases may be real, they may also be apparent pH decreases resulting from elevated concentrations of particulate and dissolved organic carbon which interfere with pH measurement.

More detailed studies of the acid-base chemistry of peatland waters before and after draining are needed.

2.2 Eh

Apparently there have been no studies on the effect of peatland drainage upon the redox chemistry of receiving waters. This is unfortunate because redox potential is as important as pH for the aqueous chemistry of N, S, Cr, Mn, Fe, Cu, Pb, and U.

3.0 CHEMICAL COMPOSITION OF DRAINAGE WATERS

3.1 Major element chemistry

3.1.1 Metals

3.1.1.1 Na, K, Mg and Ca

Since peatland drainage result in oxidation of the peat, many of the metals once found in organic matrices are released to the drainage waters. In undisturbed Soviet bogs Ca in the drainage waters ranged from 1.2-8.0 mg l^{-1} and Mg from 0.1-2.8 mg l^{-1}; mined bogs yielded 8-30 mg l^{-1} Ca and 0.5-6.0 mg l^{-1} Mg (Largin et al., 1976).

In Minnesota Na averaged 1.8 mg l^{-1} in waters draining pristine bogs whereas drainage waters from a mined bog yielded 3.0 mg l^{-1} Na (Clausen and Brooks, 1983b). In the Swedish bog Stormyran the following concentrations have been reported for K: background (pre-mining) was approximately 0.2 mg l^{-1}; after clearcutting and ditching, 0.6 mg l^{-1}; during low runoff periods following ditching (mainly mire ground-water), 0.5 mg l^{-1}; during the peat mining phase, 0.6 mg l^{-1} (Johansson and Olofsson, 1985).

The metals Na, K, Mg and Ca present no potential environmental problems upon peatland development.

3.1.1.2 Al, Fe and Mn

Since bog surface waters are acidic, relatively "reducing" and contain abundant dissolved organic matter, they are enriched in Al, Fe and Mn relative to "normal" fresh waters. Their concentrations in bog surface waters

commonly are on the order of one part per million each; in "normal" fresh waters their concentrations are approximately 0.05, 0.04 and 0.008 ppm, respectively (Appendix 1). Thus, Al and Fe are enriched by factors of approximately 100X and Mn by a factor of approximately 1000X, relative to "normal" fresh waters. These metals exceed recommended water quality concentrations for domestic water supply and for protection of aquatic life (McNeely et al., 1979). Water samples from 3 Canadian bogs were found to exceed water quality guidelines for Fe and Al in all samples from all sites (Washburn and Gillis, 1983).

Clausen (1980) reported concentrations of Al and Fe in waters draining two disturbed and two pristine peatlands. The undisturbed sites contained 0.26 and 0.08 mg ℓ^{-1} Al and 2.98 and 0.40 mg ℓ^{-1} Fe; the mined sites yielded 0.73 and 0.38 mg ℓ^{-1} Al and 4.04 and 8.16 mg ℓ^{-1} Fe. His results must be evaluated cautiously because 4 different peatland types were considered: an undisturbed fen and an undisturbed transitional peatland, a drained and mired Sphagnum bog and a drained fen.

Clausen and Brooks (1983b) calculated a mean Fe concentration of 2.64 mg ℓ^{-1} in waters draining 15 undisturbed bogs in Minnesota. The waters draining a mined bog yielded an average of 4.26 mg ℓ^{-1} Fe. The mined bog yielded less Al than the mean concentration at natural sites (0.41 vs. 0.55 mg ℓ^{-1}).

At the fuel peat mine near Cotton, Minnesota, Al, Fe

and Mn concentrations were found to decrease upon mining (Berglund et al., 1985). At control sites maximum values were 14.9 mg l^{-1} Fe, 0.8 mg l^{-1} Al and 0.74 mg l^{-1} Mn; at mined sites the values were 1.4, 0.2 and 0.24 mg l^{-1}, respectively.

A recent Swedish study confirms the observed decrease in Al and Fe concentrations subsequent to drainage (Johansson and Olofsson, 1985). Background (pre-mining) concentrations were 3.5 mg l^{-1} Fe and 0.20 mg l^{-1} Al; upon clearcutting and ditching the concentrations decreased to 1 mg l^{-1} and 0.15 mg l^{-1}, respectively. During low runoff periods following ditching (mainly mire groundwater flow) the concentrations were 1 mg l^{-1} and 0.15 mg l^{-1}, respectively; during the mining phase the concentrations decreased further, to 0.8 mg l^{-1} Fe and 0.10 mg l^{-1} Al.

In pristine bogs Al is relatively abundant because of the low pH and the abundance of dissolved organic matter; low pH and organic complexing favour Al solubility. Iron is also abundant because these waters are acidic, and the relatively "reducing" character of these waters further enhances the solubility of Fe. The Mn abundance is also attributable to low pH and relatively reducing conditions. If, when peat bogs are drained, the pH of the drainage waters increases and the peat becomes more aerobic, the solubility of Al, Fe and Mn will decrease, favouring precipitation of the metals. At Stormyran Johasson and Olofsson (1985) report finding red-brown ferric hydroxide

deposits in the ditch network. With the limited data presently available, generalizations concerning Al, Fe, and Mn in peatland drainage waters are difficult to make.

A further problem with the Al, Fe and Mn data which is available concerns the analytical methodology. Filter pore size effects can be very large, especially for metals such as Al and Fe which form colloids readily. Considering the abundance of colloidal organic matter in peatland waters, the effects of colloids on chemical analyses may be a serious problem. Until filter pore size effects are considered in these studies, comparison of data from various sources will remain difficult.

3.1.2 Nonmetals (B, C, N, P, S, Si)

The effect of peatland drainage on the organic geochemistry of natural waters is discussed elsewhere (Bourbonniere, in prep.). Here, an emphasis is placed on N, P and S. Since the majority of the N, P and S in most freshwater peats is organic, decomposition of the organic matter will result in N, P and S release to receiving waters.

3.1.2.1 Nitrogen

Low moor (fen) soils contain abundant nitrogen. In a calcareous fen soil near Braunschweig, Scheffer (1979) measured total N contents of 4.1%; he calculated 20,900 kg N/ha in the 0-20 cm (plough) layer. In an acid fen soil

near Stade he found 3% total N and calculated 11,700 kg N/ha in the plough layer. Due to relatively rapid decomposition of the peat following drainage, much more N becomes available than can be used by the agricultural crops growing there (cereals and sugar beets). In mires of northwest Germany approximately 2 cm of peat is lost each year due to decomposition, this corresponds to N losses of approximately 1000-2000 kg N/ha/yr. Nitrogen losses from the peatlands into local groundwaters have caused reductions in water quality.

Clausen (1980) found higher concentrations of total N, organic N, nitrate and ammonia in waters draining mined peatlands compared to natural sites. Clausen and Brooks (1983b) found 3.7 mg l^{-1} total N, 1.8 mg l^{-1} NH_4^+ and 1.9 mg l^{-1} organic N in the waters draining a mined bog. The mean concentrations of these species in waters from 15 undisturbed bogs were 1.5, 0.1 and 1.4 mg l^{-1}, respectively.

Piispanen and Lähdesmäki (1983) compared the organic chemistry of N in peats from mined vs. undisturbed sites. Total N in the natural peats was 8.6% vs. 6.3% for the drained peats. The drained peats had much more "soluble N", 22.4 mg kg^{-1} dry weight vs. 5.6 mg kg^{-1} for the undisturbed samples. As a result of draining, the contents of ammonia, urea and amino acids increased 4 to 7 fold, relative to the control samples.

Data for N from the High Point bog study are difficult to interpret. In waters from undisturbed sites NO_3^- ranged

from 0.005 mg l^{-1} to 1.19 mg l^{-1}, such a large range in concentration is difficult to explain. At the mined sites NO_3^- varied from 0.002 to 0.036 mg l^{-1}. Kjeldahl N at undisturbed sites was in the range 0.11 - 2.88 mg l^{-1} whereas mined sites exhibited concentrations ranging from 0.3 - 1.63 mg l^{-1}.

In their study of peat mining in North Carolina, Gregory et al. (1984) emphasized the chemistry of N and P. Waters in areas cleared of vegetation had slightly higher NH_4^+ concentrations (0.24-0.41 mg l^{-1}) than vegetated areas (0.25-0.26 mg l^{-1}). Nitrate N and Kjeldahl N were roughly the same throughout the peatland. Gregory et al. (1984) suggested that the reason why relatively little N is released upon drainage is because the peats have very high C/N ratios, for example 50:1. In other words, very little N in these peats is available for mineralization. For comparison, the calcareous fen soil discussed above had a C:N ratio of 12, and the acid fen soil had a C:N ratio of 18 (Scheffer, 1979).

The importance of C:N ratios in predicting N mineralization problems is described by Kuntze (1984). In low moor (fen) soils the peats have C:N ratios of approximately 10 and N constitutes about 3% of the dry matter; in high moor (bog) peats C:N ratios of 50-60 are common, and N makes up only 1% of dry matter. Clearly, peatland trophic status will have an important effect on the chemistry of N in the drainage waters.

In their study of a fuel peat bog in Minnesota, Berglund et al. (1985) report mean NH_4^+ concentrations of 2.8 mg l^{-1} at drained sites and 0.1 mg l^{-1} at some control sites. Kjeldahl N was 3.8 mg l^{-1} vs. 1.2 mg l^{-1} at the control sites. Nitrate N was uniformly low throughout; more than 90% of the samples contained <0.1 mg l^{-1} NO_3^-.

The effect of peat mining on the aqueous geochemistry of N is probably best illustrated by the Swedish study of Johansson and Olofsson (1985). Their data is as follows (all concentrations are approximate because they have been estimated from Figure 6 of their report):

condition of mire	total N	NH_4^+	NO_3^-
	←	$\mu g\ l^{-1}$	→
undisturbed	500	20	5
clearcutting, ditching	1100	100	50
low runoff period (mainly mire groundwater)	500	250	50
peat mining	5200	175	50

The background concentrations were determined in pore water samples collected 1m below the surface of the undisturbed mire.

Sallantaus and Pätilä (1985) point out that suspended solids in peat mine drainage waters are N-rich. During periods of disturbance, for example ditch clearing or heavy rainfall, suspended solids may reach concentrations as high as several thousands of mg l^{-1}.

3.1.2.2 Phosphorus

Clausen (1980) reported higher total P in mined vs. undisturbed peatland drainage waters. Clausen and Brooks (1983b) reported a mean concentration of total P of 0.06 mg l^{-1} in drainage waters from 15 undisturbed bogs. The mined bog they studied yielded 0.09 mg l^{-1} P on average.

At the High Point bog in Newfoundland undisturbed sites yielded 0.05-0.24 mg l^{-1} total P; mined sites yielded 0.01-0.08 mg l^{-1} (Government of Newfoundland, 1984). These data appear to suggest that the mined sites provide less total dissolved P than the pristine sites. This scenario is plausible, considering the trophic status of the mire (high pH, high concentrations of dissolved Ca): Kuntze (1984) has noted that P released from low moor (fen) soils may be immobilized as Ca phosphates.

In North Carolina total P was found to increase following peatland drainage (Gregory et al., 1984). In areas devoid of vegetation total P ranged from 0.11-0.37 mg l^{-1}; at vegetated sites total P ranged from 0.07 to 0.11 mg l^{-1}. Orthophosphate is the phosphorus form which is readily available to biota. Gregory et al. (1984) found that cleared sites ranged from 0.02-0.13 mg l^{-1} orthophosphate whereas waters draining undisturbed sites contained 0.01-0.02 mg l^{-1} orthophosphate (Gregory et al., 1984). Despite the differences between disturbed and natural sites, the authors point out that the total concentrations of dissolved P are still relatively low.

Berglund et al. (1985) drew a similar conclusion from their studies of a drained bog in Minnesota. Drained sites yielded mean total P concentrations of 0.06 mg l^{-1}; natural sites yielded 0.03 mg l^{-1}. Both of these values are within the range of concentrations of total P of waters draining undisturbed peatlands.

In a Swedish fuel peat bog total P in drainage waters was found to increase following drainage (Johansson and Olofsson, 1985). Background concentrations of total P were on the order of 20 μg l^{-1}. During the clearcutting and ditching phase total P in the drainage waters increased to 150 μg l^{-1}. During peat mining operations total P reached concentrations of 1200 μg l^{-1}. These authors note that the concentration of total P was strongly correlated with the concentration of suspended matter during both undisturbed and disturbed periods.

Sallantaus and Pätilä (1985) also found a strong relationship between contents of suspended solids and total P. Undisturbed mires yielded 18 μg P l^{-1} where as mined bogs provided 30-200 μg P l^{-1}. They found that suspended solids contained approximately 0.1% total P, and during periods of intense disturbance (heavy rainfall or ditch clearing) the concentration of suspended solids may be as high as several thousands of mg l^{-1}.

3.1.2.3 Sulphur

There are surprisingly few studies of the geochemistry of sulphur before and after peatland drainage. At the St. Shott's bog in Newfoundland the drainage waters from natural sites contained 2-6 mg l^{-1} SO_4^{2-} vs. 5-30 mg l^{-1} SO_4^{2-} at mined sites (Government of Newfoundland, 1985). The authors suggest that pyrite oxidation may be responsible for the elevated SO_4^{2-} concentrations following drainage. Although this certainly is one possibility, there is another possible explanation. Colorimetric SO_4^{2-} determinations are affected by dissolved organic carbon: highly coloured waters show higher SO_4^{2-} concentrations using this method than colourless samples. The colour of the drainage waters from the mined sites were reported to be in the range 70-700 Pt-Co units vs. 45-200 Pt-Co units for natural sites (Government of Newfoundland, 1985). If colorimetric SO_4^{2-} determinations were employed, the differences in colour may account for the apparent SO_4^{2-} differences. If SO_4^{2-} was determined using ion chromatography, then the SO_4^{2-} differences may be real. Unfortunately no details about analytical methodology are provided in the report.

3.2 Trace element chemistry

3.2.1 Metals (V, Cr, Co, Ni, Cu, Zn, Cd, Sn, Hg, Pb and U)

The concentrations of these metals in typical natural waters are as follows (Bowen, 1979):

Cd	0.1 $\mu g\ l^{-1}$	Pb	3 $\mu g\ l^{-1}$
Co	0.2 $\mu g\ l^{-1}$	Sn	0.01 $\mu g\ l^{-1}$
Cr	1 $\mu g\ l^{-1}$	U	0.4 $\mu g\ l^{-1}$
Cu	3 $\mu g\ l^{-1}$	V	0.5 $\mu g\ l^{-1}$
Hg	0.1 $\mu g\ l^{-1}$	Zn	15 $\mu g\ l^{-1}$
Ni	0.5 $\mu g\ l^{-1}$		

Thus, studies of these metals in peatland drainage waters require analytical methods capable of very low levels of detection, for example graphite furnace atomic absorption, neutron activation, etc.

Unfortunately many studies of these metals in peatland drainage waters have been performed using multi-element methods such as ICP (inductively coupled plasma emission spectroscopy); this method has relatively high levels of detection. For example Clausen (1980) used ICP for Cd, Cr, Cu, Ni, Pb and Zn, some of his results are as follows:

Cr < 0.01 - 0.02 ppm

Cu < 0.01 - 0.01 ppm

Ni < 0.04 ppm

Pb < 0.13 ppm

Such multi-element scans may be useful for determining whether or not the metal of interest is found in

concentrations greater than those recommended for the maintenance of water quality. However, when the concentrations of the metals are close to the limits of detection of the method, misunderstandings can easily develop. Brooks et al. (1982) [cited in Berglund et al., 1985] reported 0.24-0.92 mg l^{-1} Co in some peatland waters from Minnesota. In typical freshwaters Co is on the order of 0.2 $\mu g\ l^{-1}$; their values (240-920 $\mu g\ l^{-1}$) are highly anomalous and suggest nearby metal mineralization or significant anthropogenic metal contribution. Berglund et al. (1985) report < 4 $\mu g\ l^{-1}$ Co in the drainage waters from undisturbed and mined sites at the bog near Cotton, Minnesota.

Ertec Atlantic Inc. (1982) [cited in Berglund et al. (1985)] reported Pb concentrations in mire waters ranging from 0.025-1.0 mg l^{-1}. In typical freshwaters Pb concentrations are approximately 3 $\mu g\ l^{-1}$; their values (25-1000 $\mu g\ l^{-1}$) are also highly anomalous. Berglund et al. (1985) report < 6 $\mu g\ l^{-1}$ Pb in the drainage waters from pristine and mined sites at the bog near Cotton, Minnesota.

Consider once again Clausen's (1980) trace metal data shown above. The detection limit for Cr is 0.01 ppm (10 ppb); the reported concentrations range from < 10 ppb to 20 ppb. Twenty ppb Cr is high relative to its abundance in typical freshwaters approximately 1 ppb (Bowen, 1979). Using neutron activation Shotyk (1986) found 2 ppb Cr in bog surface water samples (<0.1 μm) from Luther bog in

southern Ontario. Thus, some trace element analyses of waters must be viewed cautiously. Reporting concentrations such as < 0.13 ppm Pb (< 130 ppb Pb) is not particularly helpful when typical freshwaters contain 3 ppb Pb and the recommended limit for domestic water supply is 50 ppb Pb.

At the High Point bog the concentrations of Cu and Zn in drainage waters from natural and disturbed sites have been compared (Government of Newfoundland, 1984):

	natural sites	mined sites
Cu	< 0.01-0.3 ppm	< 0.01-1.16 ppm
Zn	< 0.01-16.1 ppm	< 0.01-4.21 ppm

The maximum concentrations encountered here are very high relative to typical freshwaters, even at the undisturbed sites: 300 ppb Cu vs. 3 ppb Cu in typical freshwaters; 16,100 ppb Zn vs. 15 ppb Zn in typical freshwaters. Thus, Cu is enriched by a factor of 100X, and Zn by a factor of 1000X, relative to "normal" freshwaters. The authors concede that there may have been "sampling errors in the data set" (?) and so these data are not considered further here.

Mercury is probably the trace metal in peats which has generated the most attention as far as potential environmental impacts are concerned. Crawford (1978) expressed concern about the Hg in peats because

1) peats have tremendous capacities for adsorbing metal ions e.g. Hg^{2+} from solution and
2) coal combustion is a major source of atmospheric Hg, and many of Minnesota's peatlands are downwind

from coal burning industries and utilities.

In addition to these concerns

3) peatlands are predominantly sulphate-reducing environments, and Hg forms extremely insoluble sulphides, and

4) bacterial methylation of Hg appears to be enhanced by anaerobic, organic-rich environments (Bodaly *et al.*, 1984).

As part of his preliminary investigation of Hg in peats Crawford (1978) analyzed 8 peat samples: six had < 1 ppm Hg, one had 1 ppm Hg and one had 3 ppm Hg. These values are high relative to the concentrations reported in some Ontario peats. For example, Shotyk and Telford (1983) reported 80 ppb (0.08 ppm) Hg in the *Sphagnum* mosses growing on the surface of Galbraith bog, and < 20-50 ppb Hg (< 0.02-0.05 ppm) in the peats (*Sphagnum*, *Sphagnum*-*Carex* and *Carex* peats). The gyttja contained 50-70 ppb Hg, and the underlying clay < 10 ppb Hg (< 0.01 ppm).

Crawford (1978) noted that simply drying peat samples caused losses of Hg. Thus, drying of peat accompanying peatland drainage may result in losses of Hg from the peat to the atmosphere. The geochemistry of Hg in peats requires further investigation.

Lake sediments downstream from drained peatlands in Finland contain elevated Hg concentrations relative to lake sediments downstream from undisturbed mires (Simola and Lodenius, 1982). Lake Polvijärvi in northern Karelia is

found in a watershed containing 34.6% peatlands, 80% of these peatlands have been drained for forestry since 1960. In Polvijärvi Hg averages 0.25 $\mu g\ g^{-1}$ in the sediments (background) and increases to a maximum concentration of approximately 0.5 $\mu g\ g^{-1}$ corresponding to the year 1970. Calculations of rate of Hg accumulation through time closely corresponds to the intensity of ditching operations, reaching a maximum at the year 1970. In contrast, Paajarvi is found in southern Finland in a watershed containing 10.6% peatlands. In the sediments of Paajarvi Hg ranged from 0.032-0.088 $\mu g\ g^{-1}$. These data suggest that peatland drainage may result in Hg mobilization.

In peatland waters, Clausen and Brooks (1983b) reported 4 $\mu g\ l^{-1}$ Hg in drainage waters from a mined bog. The average Hg concentration in waters draining 15 undisturbed sites was 6 $\mu g\ l^{-1}$. Berglund et al. (1985) report much lower values in peatland drainage waters: the maximum concentration encountered was 0.9 $\mu g\ l^{-1}$ and most values were $< 0.1\ \mu g\ l^{-1}$. The drinking water standard for Hg is 2 $\mu g\ l^{-1}$.

3.2.2 Nonmetals (Ge, As, Sb, Se, Te)

Of these elements, Ge and As are potentially problematic as far as peatland drainage is concerned. Germanium and arsenic are sometimes enriched in coals (Goldschmidt 1950), and their behaviour in peat-forming

environments is poorly understood. In their study of 131 peatlands, Minkkinen and Ylirvokanen (1978) found a mean concentration of 36 ppm As in Finnish peat ashes. Samples from 4 bogs exceeded 1000 ppm in the ash and the maximum concentration of As encountered was 4800 ppm As.

Clausen and Brooks (1983b) reported 4 $\mu g\ l^{-1}$ As in waters draining a mined bog and a mean concentration of 2 $\mu g\ l^{-1}$ As in the waters draining 15 undisturbed bogs. In Ontario (Galbraith bog) and Newfoundland (High Point bog) undisturbed sites had $< 2\ \mu g\ l^{-1}$ As (Washburn and Gillis, 1983). In a separate study, the waters draining mined areas of the High Point bog were found to contain $< 5\ \mu g\ l^{-1}$ As (Government of Newfoundland, 1984). At the mined bog near Cotton, Minnesota, the drainage waters contain $< 7\ \mu g\ l^{-1}$ As (Berglund et al., 1985).

Washburn and Gillis (1983) report $< 5\ \mu g\ l^{-1}$ Sb in water samples from Galbraith and High Point bogs.

The mean concentrations of some of these elements in typical freshwaters are as follows (Bowen, 1979)

As	$0.5\ \mu g\ l^{-1}$
Sb	$0.2\ \mu g\ l^{-1}$
Se	$0.2\ \mu g\ l^{-1}$

Thus, studies of these elements in peatland waters require analytical methods capable of sub ppb levels of detection. Our understanding of the geochemistry of these elements in mires will remain poor until their total (analytical) concentrations are determined and their speciation

investigated.

4.0 RECOMMENDATIONS FOR FURTHER RESEARCH

Future studies of the impacts of peatland drainage waters upon aquatic ecosystems should at least consider these suggestions.

4.1 Site characterization

4.1.1 Complete descriptions of the vegetational ecology of the mire prior to development are necessary. Bogs and fens should be classified according to trophic status, for example, strongly ombrotrophic bog, weakly minerotrophic bog, poor fen, extremely rich fen, etc.

Based on the studies evaluated here, it appears that the pH of fen drainage waters decreases, and the pH of bog drainage waters increases, following peatland development. However, because of inadequate or uncertain site descriptions, no conclusive statements about changes in pH relative to mire trophic status can be made.

4.1.2 Complete descriptions of the hydrology of the mire prior to, during, and after development are required.

During periods of disturbance, for example, rainfall, ditch clearing, etc., the concentrations of suspended solids may be very high e.g. thousands of mg l^{-1}. Since total N and P concentrations vary with concentrations of suspended solids, the physical aspects of drainage can

explain some of the chemical aspects.

4.1.3 Complete descriptions of the peat stratigraphy are necessary. This would include peat depth, botanical composition and degree of decomposition of the peat, pH of the pore water through the profile, and nature of the underlying (mineral) material.

Many Sphagnum bogs have evolved from Carex fens; the pH of the surface waters of ombrotrophic bogs is approximately 4 whereas the pH of the pre waters of eutrophic Carex peats is approximately 8. Ditching which allows mixing of acidic surface waters with alkaline basal pore waters permits neutralization of the acidity of surface waters.

4.1.4 Descriptions of local geology would be very helpful, especially describing the mineralogy of basal sediments. For example, calcareous sediments will be much more effective in neutralizing acidic bog surface waters than siliceous sediments.

4.2 Water analyses

4.2.1 The commonest problem with the existing studies is the lack of background information. The chemistry of the drainage waters should be well characterized before development begins. These analyses should be complete (see below) and performed over a long enough period of time so that seasonal variations are well

documented.

4.2.2 In order to make intelligent conclusions about the changes in pH of drainage waters, careful pH determinations are necessary. Despite the apparent simplicity, the measurement of pH of peatland waters is very difficult to perform, a fact generally not appreciated (se Appendix 1).

Particulate organic matter and dissolved organic matter both interfere with pH measurements, and both cause an apparent lowering of pH. Studies showing decreases in pH following drainage have not convinced this author that the pH changes are not due to increases in POC and DOC. In addition, CO_2 degassing can result in pH increases.

Since pH affects metal bioavailability, careful pH studies are essential.

4.2.3 Very large differences in Al and Fe concentrations in mire waters are observed in the reports considered here. These differences may reflect inherent variability, pH differences, etc., but they also suggest that filter pore size effects may be involved.

In many studies the filter pore sizes are not reported. If the same filter pore size (e.g. 0.2 μm) was used in each study, comparisons would be easier to make.

4.2.4 Nitrogen and phosphorus have been given adequate attention. Surprisingly, sulphur hasn't. Studies of the effect of peatland drainage on the geochemistry of sulphur in mires are suggested.

4.2.5 Arsenic is known to accumulate in some peats, and germanium in some coals. Studies of these trace nonmetals in peats and peatland drainage waters would be useful.

4.2.6 Much remains to be learned about the geochemistry of trace metals in peats and peatland waters. Metals such as V, Cr, Co and Ni are relatively insoluble and are not known to accumulate in peats out of proportion with ash. These metals probably will not cause problems and their concentrations in peat pore waters are low (ppb to sub ppb). They should be determined routinely to ensure that they are below the recommended limits.

Soft acid metals such as Zn, Cd, Hg, Sn and Pb deserve greater attention. These metals form stable organic complexes, organometals and insoluble sulphides: peatlands are good environments for them to accumulate in, and peatland drainage may result in metal remobilization. In addition to the total concentration of these metals in peats and peatland waters, their speciation should be evaluated.

Uranium is commonly enriched in peats, and studies of

peatland drainage waters have overlooked this metal. Peatland drainage will favour its mobilization because oxidation enhances its solubility (see Appendix 2).

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APPENDIX A

An overview of the geochemistry of peatland waters

AN OVERVIEW OF THE GEOCHEMISTRY OF PEATLAND WATERS

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ABSTRACT - The low pH of Sphagnum bog surface waters is explained. The pH, Eh, and chemical composition of peatland waters are described. The effects of these factors on metal speciation are discussed.

PREFACE

Published studies of peatland water chemistry span several disciplines, including ecology, environmental chemistry, geochemistry and soil science, and are written in many languages, including English, Finnish, French, German, Russian and Swedish. Given such a diversity of approaches, and considering the long history of the subject, it is not surprising that misunderstandings have developed. A critical review of this extensive body of knowledge currently is underway (Shotyk, in prep.) In some ways the present report is a summary of that literature review.

For reasons of expediency it is assumed that the reader is familiar with the hydrological and botanical differences which exist between bogs, fens, marshes and swamps. The subjects addressed here include the pH, redox chemistry, chemical composition, and chemical speciation of dissolved constituents in mire waters.

INTRODUCTION

As peat in its natural state is by weight >90% water, peatlands can be viewed as a distinct class of natural water system. To understand the characteristics of any natural water system we must first consider the history of the water, and interactions of the water-rock-atmosphere systems (Stumm and Morgan, 1981).

Under the conditions of their formation all minerals are thermodynamically stable relative to their reactants. For example, igneous minerals are stable under high pressure, high temperature, anhydrous and anaerobic conditions. At the surface of the earth (low T, low P, aqueous, aerobic) these minerals are thermodynamically unstable and so they decompose, releasing solutes in the process. Thus the chemistry of natural waters is intimately related to the composition of local rocks and sediments.

Weathering reactions are acid-base reactions of the general form

i) cation-silicate + $H_2CO_3^*$ →
(solid base) (acid)

cations + HCO_3^- + $H_4SiO_4^*$ and
(dissolved salt)

ii) cation-aluminosilicate + $H_2CO_3^*$ →
(solid base) (acid)

cations + HCO_3^- + $H_4SiO_4^*$ + clay mineral
(dissolved salt)

Minerals are solid bases which combine with naturally-occurring acids such as carbonic acid, $H_2CO_3^*$. Depending on the local geology, groundwaters and surface waters contain varying concentrations of HCO_3^- as a result of such weathering reactions. In fact, the concentration of HCO_3^- can be considered a gross measure of the amount of primary minerals that have decomposed per litre of groundwater (Garrels, 1967). For example, stream waters in the Hubbard Brooks watershed, where highly metamorphosed sedimentary rocks and granites are exposed, contain approximately 1 mg l^{-1} HCO_3^- and have a pH of 4.9 (Likens et al, 1977). In contrast, a typical limestone aquifer contains 160 mg l^{-1} HCO_3^- and has a pH

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of 7.69 (Table 2). Carbonate minerals weather much faster than silicates:

iii) $CaCO_3(s) + H_2CO_3^* \rightarrow Ca^{2+} + 2HCO_3^-$
(solid base) (acid) (dissolved salt)

All other things being equal, minerotrophic peatlands in calcareous terrains should be less acidic than those in siliceous environments due to the difference in weathering rates.

All peatlands, whether ombrotrophic Sphagnum bogs (pH approx. 4) or eutrophic Carex fens (pH approx. 8), contain abundant dissolved acids from the decomposition of plant materials: carbonic acid and organic acids. Solid bases combine with H^+ produced through decay to regulate the pH:

solid base + acid → dissolved salt

Therefore, the pH of peatland waters may be controlled by the relative rates of production of H^+ (from decomposition of organic matter) and supply of bases (from local groundwaters and surface waters).

Fens, marshes and swamps all are intimately associated with groundwaters and surface waters. Thus, H^+ produced via decomposition of organic matter can be neutralized by dissolved bases and a relatively high pH can be maintained.

As peat accumulates over time, and the thickness of the peat layer increases, the degree of groundwater influence progressively decreases. Ombrotrophic Sphagnum bogs are entirely rain-fed (Gr. ombros = rain shower, trophe = nourishment). Since they receive no significant inputs of solid bases from groundwaters, the H^+ produced via decomposition is not neutralized. The result: bog waters are acidic.

In summary, ombrotrophic bog surface waters are acidic because of the lack of bases (e.g. $CaCO_3$), and their chemical composition reflects that of local precipitation.

The pH and chemical composition of minerotrophic mire waters is related to the degree of groundwater and surface water influence, and on the composition of these waters. These, in turn, reflect the physical and chemical composition of local rocks and sediments (Garrels, 1967; Garrels and MacKenzie, 1967).

THE pH OF PEATLAND WATERS

In this section I shall consider the methods of pH measurement, the pH range of peatland waters, and the cause of the low pH in Sphagnum bogs.

Methods of pH measurement

Acidity of bog waters was of interest to scientists long before the development of the pH scale by Sørensen in 1909. In studies prior to 1909 acidity of the waters was determined by titrating with a base such as 1/100 N KOH.

Until the late 1920's all the pH determinations of bog waters were performed using indicator solutions (e.g. Christopherson, 1925). The natural colour of peatland waters, ranging from almost colourless to tea-coloured, makes this method difficult to apply. Christopherson used a colour comparator: in a double testtube rack the colour standard is backed by the solution to be tested without indicator, and compared with the solution to be tested plus indicator backed by clear water. He noted that solutions of pH < 3.6 were highly coloured and this fact, in combination with the very weak colour of Bromphenol blue in this region, make it impossible to distinguish colour below this point. Another problem with this procedure is the dilution effect of the indicator on poorly buffered waters: addition of the indicator can change the pH of the sample. The sample pH will increase or decrease depending on the pH of the dye compared to the actual solution pH (Kramer and Tessier, 1982).

Potentiometric pH determination was compared with the colorimetric method (Thompson, Lorah and Rigg, 1927) and the colorimetric measurements were consistently higher. For example, in the Esperance bog potentiometric and colorimetric pH values are P 4.60, C 4.7 and C 5.1 and in the Ronald bog P 3.81, C 3.9 and C 4.3.

Quinhydrone electrodes were popular in the 30's and 40's (Pearsall and Mortimer, 1939). However, due to the acid nature of hydroquinone, and to its tendency to oxidize in alkaline solutions, this electrode is inaccurate in solutions with pH >7. Also, reducing organic substances interfere with the electrode (MacInnes, 1939).

From the late 1940's to the present day the glass electrode has been most commonly employed in peatland studies. Although most measurements are now made using the glass electrode, not all measurements are made in the same way. Some measurements are made on waters from surface pools (filtered and unfiltered), some on waters squeezed from mosses and surface peats, some directly on "moist peat". Laboratory measurements have been made on fresh (field moisture) peats, fresh peats diluted with distilled water, peats that have been dried and then re-wetted with either distilled water or a salt solution.

The difference in pH between peats and their pore waters or surface waters

was determined by Wilson et al, (1932): Sphagnum peat underlain by non-calcareous sand (peat pH 3.6, water pH 6.9); wood-reed peat underlain by Chara marl (peat pH 5.2, water pH 7.2); wood-reed peat underlain by calcareous sand (peat pH 5.2, water pH 7.2). The difference in pH between the peat and the water is due to a potential difference which exists between the surface of the peat and the bulk solution, and is caused by the carboxyl (COOH) groups on the peat (see Bates, 1973, p. 57).

In addition to the problems encountered trying to interpret the results of previous pH investigations, problems attributable to either the measuring system itself, or to the nature of the water sample, also are encountered. Most of the problems experienced during electrode pH determinations are due to the reference electrode junction (Westcott, 1978). Detailed discussions of this and other problems (stirring potentials, ionic strength effects, electrode "memory" etc) are provided elswewhere (Covington et al, 1985a,b; Davison and Woof, 1985). Here, an emphasis is placed on problems attributable to the nature of mire water samples.

Factors affecting the apparent pH of peatland waters include: the presence of colloidal and dissolved organic materials, volatile acids and oxidizable substances, time of day and temperature of the water at the time of sample collection, and the container material used for storing samples.

The "suspension effect" refers to the pH difference between a colloidal system (suspension or gel) and its filtrate, supernatant liquid or intermicellar liquid. As an extreme example, an H^+-saturated exchange resin had a pH of 0.5 whereas the supernatant solution above the "sediment" had a pH of 6.0 (Jenny et al, 1950). In addition, dissolved organic carbon can lower apparent pH; errors in H^+ activity of as much as 50% have been reported for softwater lakes (Herczeg and Hesslein, 1984). Peatland waters contain abundant volatile acids, for example CO_2 and low molecular weight organic acids (Shotyk, thesis). Losses of these acids upon sample collection, preparation, and analysis can also affect the apparent pH. Oxidation of reduced sulphur species may also be a significant source of error in the case of sulphur-rich peats.

The time of day of sample collection will be important for circumneutral samples in which midday pH values are greater than those measured in morning or evening, due to photosynthesis. Correction for temperature can be important, much more so at pH 4 than at pH 7 (Westcott, 1978). Sample container material is also important: fresh glass surfaces can contribute 20-100 μ eq l^{-1} of alkalinity (Kramer and Tessier, 1982).

Ideally, the colloidal materials present in mire water samples must be removed without losing volatile acids. An attempt to do this in waters from the Akhult mire (Sweden) was carried out by Malmer (1962). Here is an example of his results:

open water pH	4.1
"pressure" water pH	4.4
"suction" water pH	5.1

The apparent pH of the open water is probably less than the true pH due to the presence of colloidal materials. The pH measured after vacuum filtration ("suction water") is probably higher than the true pH, because volatile acids have been removed. The pH obtained using an N_2 pressure membrane extractor ("pressure water") most closely approximates the true pH of the bog water.

Clearly, further studies of the pH of mire waters are required. The dissolved species affecting the pH must be identified and appropriate methods of pH determination must be developed.

The pH range of peatland types

The pH data from Sjörs (1950) are as follows:

bog	3.7-4.2
extreme poor fen	3.8-5.0
transitional poor fen	4.8-5.7
intermediate fen	5.2-6.4
transitional rich fen	5.8-7
extreme rich fen	7-8.4

The lower limit of pH is approximately 4, typical of ombrotrophic Sphagnum bogs. These waters are probably buffered at this pH by carboxyl groups of the organic matter (see, for example, Magdoff and Bartlett, 1985).

The upper limit of pH is approximately 8.4, typical of shallow, eutrophic fens in calcareous terrains. This pH value can be interpreted in terms of calcite equilibria: $CaCO_3(s)$ in equilibrium with pure water and atmospheric P_{CO2}($10^{-3.5}$ atm) will exhibit a solution pH of 8.4. Increasing P_{CO2} 100 times (ie. $10^{-1.5}$ atm) will lower the pH to approximately 7; such high P_{CO2} values are typical for peatland waters (Websky, 1862; Shotyk, thesis). Thus the pH of these extremely rich fens can vary with P_{CO2}; sample degassing (e.g. equilibrating with the atmosphere) will cause a pH rise.

As peat accumulates over time, the thickness of the peat layer increases

and the concentration of dissolved bases in mire surface waters decreases, hence pH declines. Thus in an area of uniform geology, a strong relationship between mire surface water pH and peat thickness is expected.

The acidity of bog waters

The cause of acidity was of interest even at the time of Rennie (1810). By that time the acids that had already been found in peats included carbonic, acetic, gallic, sulphuric, suberic and the "sorreline" (=oxalic ?) acids. Reverend Rennie realized that it probably was not any one of these acids which causes the acidity of bog peats, but combinations of them. Since Rennie's time we have come to recognize four acidification mechanisms: cation exchange by Sphagnum mosses, dissolved CO_2, other inorganic acids, and organic acids.

In most cases the role of these acidifying mechanisms has been overemphasized at the expense of mire hydrology as has been convincingly demonstrated by Bellamy and Rieley (1967). They studied the chemical composition of the pore waters of a Sphagnum fuscum hummock at 4 cm intervals from its base to its apex, a total distance of 56 cm. In the bottom segment (0-4 cm) they measured 0.316 m eq l^{-1} HCO_3^- and a pH of 6.52; in the 4-8 cm section above this they found no measurable HCO_3^- and a pH of 4.22. The concentration of HCO_3^- in these waters provides an index of the amount of mineral weathering which has taken place. Their data shows that the low pH has developed in the absence of dissolved (mineral) bases. What are the acids which maintain the low pH?

a) Sphagnum mosses

In the early part of this century ecologists were intrigued by the calcifuge nature of Sphagnum mosses and this led to numerous studies of the effect of water chemistry on the growth of mosses. Toward the middle of the century this work was extended to include the effect of growing mosses on the chemistry of peatland waters.

Paul (1908) sought a classification scheme for Sphagnum mosses which would explain the distribution of species within peatlands. He found considerable overlap of species between bogs (hochmoors) and fens (niedermoors) and so he classified them on the basis of their Ca tolerance. He found a strong relationship between the acid-producing ability of the mosses and their requirement for Ca: Ca intolerant mosses are most acidic and found in bogs, while Ca tolerant species are least acidic and found in fens.

Paul (1908) realized that this acid-producing ability of the mosses might be of adaptive significance. Sphagnum mosses growing in fens have a relatively plentiful supply of Ca from groundwaters and surface waters. Ombrotrophic bog species receive all their nutrients from atmospheric deposition plus recycling. Paul concluded that the acid of the mosses must be the solvent whereby the moss obtains its nutrients from dust.

Chodat (1924) noticed that the waters squeezed from mosses were more acidic than the waters surrounding the mosses, and that the occurrence of Sphagnum corresponded to the occurrence of low pH values. Kurz (1928) measured pH through a vertical peat profile. At the surface of the Hartford bog (Sphagnum peat) he found a pH of 4.0, the pH increasing with depth until he encountered lake muds of pH 8.4. The author wrote that this profile "demonstrates the importance of Sphagnum as an acidifier of bogs" (p. 58, 1928).

The ability of Sphagnum to remove cations from solution in exchange for H^+ as a metabolic necessity was extended to explain the mechanism by which bogs became acidic. Even today, Sphagnum mosses are considered by some to be responsible for the low pH of bogs. However, most workers now agree that cation exchange by Sphagnum mosses contributes to the low pH, but is by no means the sole cause.

b) Dissolved CO_2

The presence of carbonic acid in peat waters was well established by the time of Rennie (1810). The first modern study of CO_2 in relation to the pH of bog waters appears to be that of Stremme (1908). He found that the acidity of bog waters collected near Berlin varied with the temperature at the time of collection; acidity decreased with increasing water temperature. When $Ba(OH)_2$ was added to the waters, a precipitate formed; this effervesced upon addition of acid. Furthermore, the waters were no longer acidic after boiling. These observations led Stremme to conclude that carbonic acid controlled the pH of these waters.

A more convincing study was performed in the United States by Thompson, Lorah and Rigg (1927). They measured dissolved CO_2 in bog waters and calculated the pH expected from the measured concentration ($pH = 3.9 - \frac{1}{4} \log P_{CO_2}$, P_{CO_2} in atm.); this calculated pH was compared with pH values measured potentiometrically and colorimetrically. Dissolved CO_2 ranged from 68.3 to 76.9

ppm in the Esperance bog and the calculated pH from 4.67 to 4.64. The measured pH values were 4.60 (potentiometric) and 4.7-5.1 (colorimetric). Thus, for this bog at least, the measured concentration of dissolved CO_2 is sufficient to explain the low pH. However, in the Ronald bog these authors recorded pH values too low to be explained by CO_2 alone: dissolved CO_2 ranged from 33.8 to 55.8 ppm and the calculated pH from 4.82 to 4.71. The measured pH values were 3.81 (potentiometric) and 3.9-4.3 (colorimetric). Clearly, there is enough CO_2 in some bogs to explain the low pH, but not in all.

c) Other inorganic acids

In a study of British bog surface waters a very strong correlation was shown to exist between H^+ and SO_4^{2-}, r = 0.985 (Gorham, 1958). The lowest pH values were recorded near major industrial areas and the highest values in pristine sites; apparently sulphuric acid is an important acid in polluted bog surface waters. In minerotrophic peats enriched with metal sulphides, sulphide oxidation will cause dramatic decreases in pH.

In the surface waters of "normal" Sphagnum bogs, sulphate is on the order of 1 mg l^{-1} and cannot be very important in the acid-base chemistry. Surface peat pore waters are SO_4^{2-}-rich, on the order of 10-15 mg l^{-1}, probably the result of decomposition of organic matter (Shotyk, thesis); here SO_4^{2-} may be much more important in this regard.

d) Organic Acids

The presence of acetic, gallic, suberic and the sorreline acids was well known by the beginning of the 19th century (Rennie, 1810). The first quantitative investigation of dissovled organic matter appears to be that of Thompson, Lorah and Rigg (1927). They measured the colour intensity of some Pugent Sound bog waters with a Lovibond tintometer using yellow glass standards. The waters ranged in colour from light to deep yellow and there appeared to be a relationship between water colour and pH. Measurements of dissolved organic matter showed that

(% organic matter) x (pH) = constant

Charge balance analyses performed on water samples from Thoreau's bog showed that the sum of inorganic cations exceeded that of inorganic anions by a factor of approximately 2 (Hemond, 1980). Following UV irradiation, the cation and anion sums were essentially equal, clearly demonstrating the importance of organic acids in Thoreau's bog.

THE REDOX CHEMISTRY OF PEATLAND WATERS

The presence of "carburetted hydrogen" (CH_4) and "sulphuretted hydrogen" (H_2S) in peat bogs was already well known by the early 1800's (Rennie, 1810). Quantitative studies of the composition of the dissolved gases in mire waters appeared later on in that century and clearly established the "reducing" nature of these ecosystems.

Oxidation-reduction processes affect the geochemistry of C, N, S, V, Cr, Mn, Fe, Cu, As, Mo, I, Au, U and some of the platinum group elements. For simple inorganic systems (e.g. one element dissolved in pure water), the pH (hydrogen ion activity), and the pe (electron activity) can be considered two complementary master variables.

However, despite the geochemical importance of oxidation-reduction processes, studies of the pH of peatland waters greatly outweigh investigations of redox chemistry. Some of the reasons for this imbalance, and possible solutions, are provided here.

Redox characteristics of natural waters

In a simple redox cell the electron activity is proportional to the ratio of oxidized to reduced species. For example, at 25°C

$$Eh = E^\circ + \frac{0.059}{n} \log \frac{(oxid)}{(red)}$$

where Eh = measured potential of the reaction
E° = standard electrode potential for that reaction
n = number of electrons transferred during the reaction
(oxid), (red) = activities of the oxidized and reduced species, respectively

By measuring the Eh of a simple redox cell, the ratio of the activities of the oxidized and reduced species can be calculated. Unfortunately, natural water systems are dynamic and true redox equilbrium is not possible for a number of reasons:

i) many redox reactions are extremely slow
ii) natural systems are not "closed". There is a continual input of photosynthetic energy (for example, in peat bogs organic carbon is produced faster than it can be destroyed)

iii) many redox reactions are biologically mediated, for example sulphate reduction. Thus the extent to which these reactions are driven depends on biological activity

iv) redox reactions often proceed independently of one another, i.e. there is no equilibrium.

These and other problems are discussed by Morris and Stumm (1967) and Stumm and Morgan (1981).

The state of disequilibrium was demonstrated recently by Lindberg and Runnells (1984). Over 600 previously published, high quality water analyses from various geographic areas were carefully examined. For each sample, pH, measured Eh and the activities of at least one pair of redox couples was available, for example Fe^{3+}/Fe^{2+}, HS^-/SO_4^{2-}, NO_2^-/NO_3^-, CH_4/HCO_3^-, etc. They compared the measured Eh with the Eh calculated from the various redox couples of the corresponding water sample. None of the computed Eh values agreed with the measured Eh.

Like pH measurements, Eh determinations, despite their apparent simplicity, are difficult to perform and interpret (Stumm and Morgan, 1981). Ideally, the Eh electrode is chemically inert (e.g. Pt), and acts only upon the electrical potential of the system. Dissolved species that will react chemically with the Pt surface, for example hydrogen sulphide, oxygen and some organic substances, may "poison" the electrode (Whitfield, 1974). Disturbing the sample, causing release or absorption of O_2, H_2S etc. also will affect the measured potential. Additionally, the problems encountered with reference electrode junctions described earlier (for pH measurement) also apply to Eh measurement.

Despite the theoretical and practical problems outlined above, and others described elsewhere (Stumm and Morgan, 1981), the concept of a redox potential is very useful in geochemical studies of redox-sensitive elements. Rather than measure Eh, analytical determinations of individual redox species of interest (e.g. HS^-, SO_4^{2-}) would be illuminating.

Redox chemistry of peatland waters

In addition to Eh measurements, qualitative tests for the presence of ferrous iron, nitrate, ammonia, sulphate and sulphide in peats were performed by Pearsall and Mortimer (1939). They defined "oxidizing" as peats yielding negative ferrous iron, positive nitrate, and positive sulphate tests, and "reducing" as peats with positive ferrous Fe, positive ammonia and positive sulphide tests. The distinction between the two corresponds to approximately 0.5 mg l^{-1} dissolved oxygen.

A surprising result was obtained through a Sphagnum bog profile: the surface Sphagnum peats were more reducing (43-91 mV) than the Eriophorum peats (448-456 mV) at a depth of 320-400 cm (Gorham, 1949). It is possible that the Pt electrode had become contaminated by an iron oxide, causing high apparent potentials. It is also possible that some basal peats are more oxidizing than peats just below the mire surface, as in the case of this has been reported in some Finnish peatlands (Puustjarvi, 1952).

In the sloping mire Korteaapa, Puustjarvi (1952) found measurable ferric iron in the surface layer and in the basal peat layer, but not in the middle tier. The "oxidizing" character of surface peats is readily explainable in terms of the diffusion of atmospheric oxygen into the surface water. Puustjarvi explained the "oxidizing" conditions at depth due to the presence of dissolved oxygen in groundwaters. Thus it may be that some bogs are "oxidizing" at the top and bottom, but "reducing" in the middle.

Many peat bogs have poorly decomposed (H2-4) surface and basal peat layers, and well decomposed (H5-8) middle layers. For example, the Luther bog north of Guelph, Ontario, has been described as follows: the top 50 cm is H3 Sphagnum-dominated peat; the middle 300 cm is H4-8 Sphagnum-dominated peat; the bottom 200 cm is H3-4 Carex-Scheuchzeria peat (Shotyk and Glooschenko, in prep.). The hydraulic conductivity of H3-4 Carex peat is approximately 1000 times greater than H8 Sphagnum peat. In recharge areas with sandy or gravelly soils, shallow groundwaters commonly contain measurable dissolved oxygen (Freeze and Cherry, 1979). In light of these facts, Puustjarvi's explanation of the ferric iron profile at Korteaapa seems plausible.

CHEMICAL COMPOSITION OF PEATLAND WATERS

For mire waters there have been very few studies of the geochemistry of individual elements per se. From the published analyses, and considering mire hydrology and general geochemical principles, some generalizations can be made. First, since ombrotrophic Sphagnum bogs are fed entirely by atmospheric deposition, the composition of bog surface waters approach rainwater composition (Table 1). Second, since the waters of minerotrophic mires (fens, marshes and swamps) reflect the

composition of local groundwaters and surface waters, the chemistry of these waters depends upon the texture and mineralogy of local rocks and sediments (Table 2).

	Rainwater (1)	Rainwater (2)	Rainwater (3)	Bog surface water (4)	Bog surface water (5)	Bog surface water (6)
Na	0.12	0.57	0.63	0.25	0.6	1.7
K	0.07	0.09	0.09	0.23	1.3	0.7
Mg	0.04	0.07	0.09	0.28	1.0	0.5
Ca	0.16	0.86	0.5	0.70	2.4	2.3

1 Likens et al (1977) for bulk precipitation, Hubbard Brook Experimental Forest, West Thornton, New Hampshire

2 Pierson and Taylor (1983) for rainwater, Telford Watershed, Peterborough, Ontario

3 Verry (1983) for bulk precipitation, Marcell Experimental Forest, north-central Minnesota

4 Gorham et al (1985), mean values for surface waters from 14 continental bogs

5 Verry, 1975

6 Schwintzer and Tomberlin, 1982

Table 1 Major metallic cations in rainwater vs bog surface water (mg l^{-1})

	River (1)	Stream (2)	Groundwater (3)	Fen (4)	Fen (5)	Swamp (6)
Na	6.3	0.9	7.9	2.0	2.7	2.8
K	2.3	0.2	1.0	3.1	0.5	0.9
Mg	4.1	0.4	12	2.9	10.5	14.2
Ca	15	1.7	56	16.6	44.5	83.6
HCO_3	58.4	0.9	180	54.2*	153*	267*

1 Mean world river water (Livingstone, 1963)

2 Stream water, Hubbard Brooks watershed, pH 4.92 (highly metamorphosed sedimentary rocks - mudstones and sandstones, and granites - Likens et al 1977).

3 Limestone aquifer, Florida, pH 7.69 (Freeze and Cherry, 1979).

4 Fen (Verry, 1975)

5 Fen (Schwintzer and Tomberlin, 1982)

6 Hardwood swamp (Schwintzer and Tomberlin, 1982)

* Total alkalinity expressed as $CaCO_3$ (mg l^{-1})

Table 2 Major metallic cations and bicarbonate in various natural waters (mg l^{-1})

Major metallic cations

Na, K, Mg and Ca

The following data have been conveniently summarized by Gorham (1955).

peatland type	total concentration of major elements, Na + K + Mg + Ca (mg l^{-1})
raised bog	3.3
extremely poor fen	4.4
poor fen	6.4
transitional poor fen	9.7
rich fen	10.9
transitional rich fen	28.8
extremely rich fen	53.4

Bog surface waters reflect the composition of precipitation, thus Na is a relatively important cation. Rich fens reflect the composition of telluric waters, thus Ca is relatively more important. As peat accumulates over time, and as the degree of groundwater influence progressively decreases, the relative importance of Na will increase at the expense of Ca.

The concentration of cations in bog surface waters depends on several factors, including weather effects and proximity to oceans. During dry periods dissolved constituents in bog surface waters may be more concentrated than during wet periods by as much as a factor of 2 (Gorham, 1956). Seasonal and spatial variability of dissolved metals was reported for some bog waters by Summerfield (1974).

The influence of sea spray on the chemical composition of bog surface waters was illustrated by Gorham and Cragg (1960). In these Falkland Island waters Na, K, Mg and Ca ranged from 26-63, 0.7-3.5, 3.3-9.8 and 1.3-3.2 ppm, respectively. By correcting for Cl^- the authors determined the proportion of these metals supplied by the sea: Na 100%, Mg 90%, K 80%, Ca 70%.

The abundance of major element cations in minerotrophic peatland waters depends very much on the local geology. For example, in the Hubbard Brooks watershed, underlain by highly metamorphosed sedimentary rocks and granites, the streams contain approximately 0.5 mg l^{-1} Mg and 2 mg l^{-1} Ca (Table 2). In contrast, a limestone acquifer in Florida has 12 mg l^{-1} Mg and 56 mg l^{-1} Ca (Table 2). Thus some minerotrophic mire waters approximate rainwater in their chemical composition, pointing to a geological control on the vegetational ecology of mires. In north central Alberta a minerotrophic fen underlain by unconsolidated gravels and quartzitic cobbles showed a mean pH of 5.2 and mean Ca content of 2.3 ppm (Vitt et al, 1975). In minerotrophic fens in calcareous terrains of western Alberta the pH varied from 6.8-7.9 and Ca from 18-37 ppm (Slack et al, 1980). These observations can be explained by considering rates and products of mineral weathering.

Since carbonate minerals are very soluble, groundwaters in calcareous terrains contain abundant Mg and especially Ca. Calcite in equilibrium with pure water and atmospheric P_{CO2} ($10^{-3.5}$ atm) will produce a solution bearing 20 ppm Ca. Increasing P_{CO2} by a factor of 100 (to $10^{-1.5}$ atm, more representative of mire waters) will increase the concentration of Ca in solution to 100 mg l^{-1}. Thus peatlands in calcareous terrains are able to

sustain even the most nutrient demanding wetland plant species.

In mafic terrains, Ca and Mg will be less abundant, but still in good supply; mafic rocks such as basalts contain abundant olivine, pyroxene and Ca-feldspar, relatively unstable minerals which provide Ca, Mg and Fe as solutes.

In felsic terrains Ca and Mg will be much less abundant in groundwaters; consider the Hubbard Brooks watershed noted above. Felsic rocks such as granites are dominated by quartz and K-feldspar; these minerals are relatively stable under earth surface conditions. Magnesium and Ca are provided only by accessory minerals such as hornblende and biotite, respectively. In fact, felsic rocks such as granites contain 1/4 as much Ca and 1/10 as much Mg as mafic rocks such as basalts (see Shotyk, this volume, Table 2).

Excellent descriptions of the principles and mechanisms controlling the composition of freshwater in igneous terrains are provided by Garrels (1967) and Garrels and MacKenzie (1967).

Al, Mn and Fe

Peat bog waters are acidic, relatively "reducing", and contain abundant dissolved organic matter. For these reasons bog surface waters are enriched in Al, Mn, and Fe relative to "normal" freshwaters. For example, in waters from some bogs in Virginia, Robinson (1930) found 1-2 ppm Al, 1-7 ppm Mn (expressed as MnO) and 1-40 ppm Fe (expressed as Fe_2O_3). In typical freshwaters their concentrations are Al 0.05 ppm, Mn 0.008 ppm, and Fe 0.04 ppm (Drever, 1982).

A seasonal variation in concentration of these elements has been demonstrated by Summerfield (1974). In the Wem Moss raised bog Fe varied from <0.1-1.6 ppm. Spatial variablity is also considerable. In areas of low rates of water flow Fe and Mn are more abundant than in faster moving waters. Sparling (1966) found that Fe decreased from 0.40 to 0.005 mg l^{-1} and Mn decreased from 0.32 to 0.001 mg l^{-1} as flow rate increased from 0.24 cm s^{-1} to 8.6 cm s^{-1}. Corresonding to the increase in flow rate was an increase in percent oxygen saturation, from 30 to 90 percent.

The iridescent, "oily" film characteristics of chalybeate waters is commonly observed on mire surface waters (Robinson, 1930; Pearsall and Mortimer, 1939; Puustjarvi, 1952). The formation of this film is attributed to the oxidation of ferrous carbonate to ferric hydroxide (see Shotyk, this volume).

Trace metals

The trace element chemistry of bog surface waters depends to a great extent on the composition of precipitation and dry deposition. For lithophile metals such as Ti, V, Cr, Mn, Fe, Co and Ni, except where there are local sources to the atmosphere, relatively little variability in atmospheric deposition is expected. For the atmophile elements Cu, Cd, Zn, Sb, Mo, Ag, Hg, and Pb, the anthropogenic fluxes tp the atmosphere greatly exceed the natural fluxes (see Shotyk, this volume, Table 1). Atmospheric deposition of these metals will vary with the degree of human activity. Unfortunately, studies of trace metal chemistry of bog surface waters in relation to atmospheric deposition have yet to be performed. In fact, trace metal data for bog waters is scarce. In ombrotrophic bog surface waters Tolonen and Seppanen (1976) found approximately 1 ppb Mo, 10 ppb Cu and 30 ppb Zn; Shotyk and Glooschenko (in prep.) report 1 ppb V, 2 ppb Cr and 0.5 ppb U. Data are completely lacking for metals of the second and third transition series, the lanthanides, and metalloids.

Geological controls on the trace element chemistry of minerotrophic mires are expected to be significant. For example, compare the abundances of Cr, Cu and Ni in typical granites and basalts (mg/kg): Cr 20 vs 200, Cu 10 versus 100, Ni 1 vs 150 (see Shotyk, this volume, Table 2). Some relationships between geology and trace element chemistry of minerotrophic peatland waters are described by Shotyk (this volume). However, most of the mires discussed there are unusual in that their metal contents are highly anomalous, reflecting local metal mineralizations.

Inorganic nonmetallic species

In an ombrotrophic Sphagnum bog in Massachusetts the mean NO_3^- concentration was reported as 45 μ eq l^{-1} (2.8 mg l^{-1}) and mean NH_4^+ as 90 μ eq l^{-1} (1.6 mg l^{-1}) (Hemond, 1980). The mean SO_4^{2-} concentration for surface waters of 14 continental bogs is 15.4 μ eq l^{-1} (0.7 mg l^{-1}) (Gorham et al, 1985). The mean value for surface waters in Luther bog, north of Guelph, Ontario is approximately 1 mg l^{-1}; surface peat pore waters contain 10-15 mg l^{-1} (Shotyk and Glooschenko, in prep.).

The major element chemistry of surface waters from bogs, fens and swamps has been compared by Schwintzer and Tomberlin (1982). Total dissolved P in hardwood swamps is approximately 0.17

mg l^{-1}, in bogs 0.15 mg l^{-1}, and in fens 0.03 mg l^{-1}. Total Si ranges from 0.3 mg l^{-1} in bogs and 3.8 mg l^{-1} in hardwood swamps to 7.0 mg l^{-1} in fens.

Total dissolved B in mire waters is on the order of 30 μ g l^{-1} (Tolonen and Seppanen, 1976) and F^- probably 10 μ g l^{-1} (Shotyk and Glooschenko, in prep.).

Elements such as As, Se, Te, Br, and I, and ions such as CN^-, SCN^-, etc, are yet to be investigated.

Organic species

The organic matter of soils, sediments and natural waters can be divided into two broad categories: humic and non-humic substances. Humic substances are extremely complex biopolymers that result from the chemical and biological degradation of plant and animal remains, and from the synthesizing ability of microbes. Non-humic organic materials are less complex and have clearly recognizable chemical and physical properties. Amino acids, aliphatic carboxylic acids, phenolic acids and simple sugars are examples of non-humic organic material.

Recent studies of the distribution of dissolved organic matter in seawater show that two-thirds of the DOM has molecular weights <1000 (Carlson et al, 1985). Here I assume a similar DOM distribution for peatland waters and I emphasize the geochemistry of non-humic organic acids. Readers interested in the chemistry of humic materials in bog waters should refer to the recent study by McKnight et al (1985).

Some of the soluble constituents of 14 species of Sphagnum were identified by Maas and Craigie (1964). The dominant organic acids were usually malic, citric, and sometimes oxalic; they also found succinic and fumaric acids. Of these acids, only oxalic acid has been quantitatively identified in peatland waters. In the porewaters of Luther bog, oxalate ranges from approximately 0.1 to 0.5 mg l^{-1} (Shotyk and Glooschenko, in prep.). Oxalate and sulphate in the pore waters are strongly correlated ($r=0.92$), suggesting a redox control of oxalic acid.

The dominant organic acids in waterlogged mineral soils are reported to be formic, acetic, butyric and propionic acids (Ponnamaperuma, 1972). Considering the gross similarities between waterlogged soils and peat-forming environments, these acids should also be abundant in peatland waters. As much as 0.5 mg l^{-1} acetic acid has been reported in fresh bog water samples (Shotyk and Glooschenko, in prep.). In addition, in water samples which had been stored for 10 days @ 4° C, up to 1 mg l^{-1} formic acid was detected. The formate could not be identified in fresh samples, so its presence in stored samples may be an artefact of decomposition.

Low molecular weight aliphatic acids may contribute significantly to the low pH of bog surface waters. Consider the first pK_A of these acids: maleic 1.94, pyruvic 2.49, oxaloacetic 2.56, malonic 2.86, fumaric 3.03,and citric 3.13. Clearly, the geochemistry of these acids requires further study.

Phenolic acids such as p-hydroxybenzoic, p-coumaric and vanillic acids have been identified in waterlogged soils. Protocatechuic, gentesic and gallic acids have been identified in the soil solutions of some podzolic soils (Evans, 1980). These are weak acids (in terms of their dissociation constants) and so may not figure significantly in the acid-base chemistry of mire waters. However, they form extremely stable metal complexes, for example with Al, Fe, Cu and U, and therefore deserve further attention.

SPECIATION OF DISSOLVED CONSTITUENTS IN MIRE WATERS

Introduction

The speciation of a metal refers to the distribution of a metal among its various (soluble) complexed states. It is the activity of individual species, rather than the total (analytical) concentration of a dissolved element, which determine solubility, toxicity and availability. In peatland waters it is reasonable to expect organic complexing of metals to affect the distribution of dissolved species.

Ombrotrophic bog surface waters are ideal for studies of metal-organic interactions because

i) they are enriched in dissolved organic carbon (DOC) relative to "normal" freshwaters; DOC is on the order of 30-70 mg l^{-1}
ii) they are depleted in Mg and Ca relative to "normal" freshwaters, thus organic ligands are relatively more available to complex other metals
iii) they are enriched in Al and Fe relative to "normal" freshwaters, thereby increasing the likelihood of organic complexing of these two metals
iv) they are relatively free of suspended inorganic solids e.g. clays

It is a common misconception that simple organic molecules are "probably quantitatively insignificant in natural aqueous systems" as far as metal-organic chemistry is concerned. It certainly is

true that the concentrations of dissolved, free, low molecular weight organic molecules in natural waters are low. For example, in peatland waters individual, free, dissolved amino acids are on the order $\mu g\ l^{-1}$ (Baker et al, 1982). However, some of these molecules form extremely stable complexes with specific metals, for example the glycine complex of Pd, the p-aminosalicyclic acid complex of U, etc (Shotyk, 1984). Thus it is necessary to consider the product

(concentration of ligand) x (stability constant of complex)

rather than simply the abundance of the ligand alone, to assess the importance of complexation by these ligands.

In order to evaluate the effect of an individual ligand on the distribution of dissolved species, one must consider all possible chemical interactions among all species present. Computers are required to perform such calculations.

Speciation calculations

The speciation of dissolved constituents in bog and fen surface waters has been calculated using the computer program GEOCHEM (Shotyk, thesis; Shotyk and Glooschenko, in prep.). GEOCHEM considers complexation, precipitation, oxidation-reduction, cation exchange and metal ion adsorption equilibria for up to 36 metals and 69 ligands. It is described in detail in the GEOCHEM manual (Sposito and Mattigod, 1979). Caveat: the results of calculations performed using computer programs such as GEOCHEM are only as good as the data used to make them. Input data for the calculations were obtained as follows: Na, Mg, Ca, Al, V, Cr, Mn, Zn and U by neutron activation, CO_2 by gas chromatography, Cl^-, SO_4^{2-}, acetate, formate and oxalate by ion chromatography (Shotyk, thesis). Potassium, Fe, NH_3^*, PO_4^{3-} and amino acid concentrations are taken from literature values; Ni, Cu, Pb, citrate, tartrate and salicylate are estimated values. In total 13 metals and 27 ligands are considered.

Results of the speciation calculations

A detailed discussion of the results is provided elsewhere (Shotyk, thesis). Here, a few of the salient features are considered. Hopefully, these comments identify some of the gaps in our knowledge of the chemistry of mire waters.

At pH 4 (ie. bog surface water conditions), with Al, Fe, oxalate, citrate and tartrate each equal to 500 $\mu g\ l^{-1}$ (0.5 ppm), 50% of the total Fe and 20% of the Al is bound by these three organic acids. It is most likely that these calculations underestimate the extent to which Al, Fe and other metals are organically bound. The utility of the calculations will improve when more data concerning the abundance of organic ligands, and the stability of metal-organic complexes, becomes available.

At pH 8 (ie. rich fen water composition) amino acids such as glycine and alanine are important sequestering agents for Cu, despite their low total concentration, (<10 $\mu g\ l^{-1}$). Since P_{CO2} ($10^{-1.5}$ atm) and pH are high, carbonato complexes of Cr, Cu, Fe, Ni, Zn, Pb and U are significant. Hydroxo ligands are also important, for example for Al. Once again, the extent of organic complexing probably is underestimated, due to the lack of input and stability constant data.

Phosphate, ammonia and fluoride are potentially important ligands in mire waters: PO_4^{3-} for Cr and U, F^- for Al and U, and NH_3 for Cu. In order to better understand chemical speciation in peatland waters, more of the following data is needed:

i) abundance of dissolved metals, especially trace metals such as Ni and Co, and ultra trace metals such as Ag, Cd and Hg.

ii) abundance of dissolved ligands: inorganic species such as PO_4^{3-}, F^-, CN^-, SCN^-, etc, and organic species, especially aliphatic and aromatic carboxylic acids.

iii) stability constants of metal-organic complexes.

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APPENDIX B

An overview of the inorganic chemistry of peats

AN OVERVIEW OF THE INORGANIC CHEMISTRY OF PEATS

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ABSTRACT - The geochemistry of Al, Si, Na, K, Mg, Ca, Cr, Cu, Fe, Mn, Ni, Pb, U, V and Zn in peats is described. Factors affecting the supply of metals to peatlands (atmospheric deposition and local geology), and metal redistribution within mires (pH, Eh, sulphate reduction, organic complexing and plant bioaccumulation) are described.

PREFACE

Most of the work on the inorganic chemistry of peats can be divided into 4 categories:

1) geochemistry, mainly from the point of view of geochemical exploration for mineral deposits,
2) ecology, in an effort to better understand the relationship between the nutrient status of peats and the distribution of living plants in undisturbed mires,
3) soil chemistry, with particular reference to nutrient availability in the plough layer of drained organic soils, and
4) environmental chemistry, using surface peats in ombrotrophic bogs as monitors of atmospheric metal deposition.

From a survey of the literature it is apparent that the geochemists and soil chemists have largely overlooked the extensive literature on peatlands published by the ecologists, and the ecologists have returned the compliment! This problem, coupled with the lengthy history of the subject, has resulted in some misunderstandings. A critical review of the literature currently is underway (Shotyk, in prep.). This paper is in some ways a brief summary of that review. Here, an emphasis is placed on the sources of inorganic elements (Al, Si, Na, K, Mg, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb, and U) to the peatland and processes controlling their subsequent remobilization.

INTRODUCTION

Since ombrotrophic Sphagnum bogs depend entirely on atmospheric deposition for their inorganic constituents, the chemical composition of precipitation and dry deposition (dust) are of paramount importance to the chemistry of bog peats. Atmospheric interference factors are calculated as (total anthropogenic emissions ÷ total natural emissions) x 100% (see Table 1, taken from Lantzy and MacKenzie, 1979). A value of 100% means that the anthropogenic and natural fluxes are equal. For example, natural sources of Al to the atmosphere are approximately 7 times as important as anthropogenic sources; for Pb, anthropogenic sources are approximately 35 times as large as the natural flux. This suggests that Al in mosses and surface peats should vary only with ash content whereas Pb will vary with proximity to human activity.

Element	Atmospheric Interference Factor (%)	Element	Atmospheric Interference Factor (%)
Al	15	Sn	821
V	19	Cu	1,353
Fe	39	Cd	1,697
Mn	52	Zn	2,344
Cr	181	As	2,786
U	323	Hg	27,500
Ni	344	Pb	34,383

Table 1. Atmospheric interference factor of several elements (see text for definition. From Lantzy and MacKenzie, 1979).

Minerotrophic mires (fens, marshes and swamps) are intimately associated with groundwaters and surface waters, hence the composition of local rocks

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will directly influence the chemical composition of these peats. Minerotrophic peats in basaltic terrains should contain far more Al, Fe, Na and Mg, and far less Ca, than peats in limestone regions (Table 2). This applies to trace elements as well; compare Ni in granites (1 ppm) with basalts (150 ppm). In addition, peats in areas of mineralized bedrock should reflect metal anomalies. Atmospheric deposition of metals to minerotrophic mires is also important for the atmophile elements (Sn to Pb in Table 1).

Element	Crust[1]	Granite[1]	Basalt[1]	Limestone[2]
Al	81,000	77,000	86,000	8,000
Fe	50,000	27,000	85,000	17,000
Ca	41,000	15,000	72,000	340,000
Na	24,000	29,000	19,000	1,300
Mg	21,000	4,000	45,000	5,000
K	21,000	32,000	8,000	3,100
Mn	1,000	500	1,700	620
V	110	90	250	45
Cr	100	20	200	11
Ni	75	1	150	7
Sn	50	50	200	20
Co	50	13	100	4
Pb	15	20	6	5
U	2.7	5	0.5	2.2

1. Brownlow (1979); 2. Bowen (1979).

Table 2 Typical abundance of metals in the earth's crust, and various rock types

INORGANIC CHEMISTRY OF PEATS

The inorganic chemistry of peats has conveniently been summarized by Naucke (1980) and some of his findings are presented in Table 3.

		pH	Ash (%)	N (%)	Mg	Ca	Al	Fe	Cr	Co	Mn	Ni	Pb	Zn
Hochmoor (bog)	min	3.5	1.0	0.08	0.2	0.02	0.03	1	2	6	2	2	3
	max	4.5	5.1	0.27	0.4	0.34	0.47	28	30	91	60	60	50
	mean	4	3.0	0.16	0.3	0.15	0.24	16	9	39	15	23	23
Niedermoor (fen)	min	5	33	0.10	2.0	0.3	0.1	30	9	140	20	2	24
	max	7	96	0.68	4.0	1.7	2.6	130	29	420	66	83	106
	mean	6	35	0.39	3.0	1.0	1.7	80	18	260	43	62	66

Table 3 Chemical composition of highmoor and lowmoor peats (from Naucke 1980). Data expressed as percent or parts per million (mg/kg) of peat (dry weight basis).

Nitrogen, sulphur and phosphorus are rarely greater than 1, 0.25 and 0.1% of the dry weight of hochmoor (bog) peats, respectively. In niedermoor (fen) peats N ranges from 2.5-4.5% and S from 0.5-5.0%. Naucke also provides the following range in the composition of peat ash, with the lower limit representing pristine hochmoor peats:

SiO_2	10-45%	MnO	0.1-0.3%
Al_2O_3	1-11%	K_2O	0.1-2.5%
Fe_2O_3	1.5-5.5%	Na_2O	0.2-5%
CaO	2-45%	P_2O_5	1-3%
MgO	1-20%	SO_3	5-20%

In general, metal profiles through peat bogs often have a distinct "C" shape: metal concentrations are greatest at the top and bottom of the bog, and lowest in the middle. This is especially true of bioessential elements (see, for example, Sillanpaa 1972). The upper zone ("torfogeneschict") is the aerobic zone of active plant growth and peat accumulation. In this zone the maximum concentrations of a few metals are found, for example K and Pb: the K maximum is due to plant concentration and the Pb maximum to anthropogenic atmospheric deposition.

The middle zone ("grenzschicht") is completely anaerobic and the minimum concentrations of metals are found here. Above and below this zone the concentrations of metals increases.

The maximum metal concentrations are usually found in the basal peat layer, usually but not always, because of the high ash content. For example, Ni maxima here correspond with ash content, but U is enriched out of proportion with ash, suggesting geochemical enrichment (reduction of UO_2^{2+} to $UO_2(s)$, adsorption of UO_2^{2+} by organic matter, etc.).

Another important zone in mires is in between the torfogenenschicht and the grenzschicht, and corresponds to the zone of water table fluctuation. Recently several authors have reported peaks of metal concentration here, especially for Al, Fe, Zn and Pb. The most important factors affecting metal solubility here are the changes in redox potential, sulphate reduction, and changes in pH. The redox potential will drop significantly on going from the aerobic surface peat, through the water table to the anaerobic peat. The decrease in redox potential is probably large enough to cause precipitation of copper as native Cu. Biological sulphate reduction will cause Zn and Pb to precipitate as insoluble sulphides. An increase in alkalinity is expected to accompany the reduction of sulphate:

$$SO_4^{2-} + 2CH_2O \rightarrow 2HCO_3^- + H_2S$$

The alkalinity generated will increase the pH, thereby decreasing the solubility of Fe and Al(precipitation as insoluble hydroxides).

Part of the explanation of the "C" shape is due to the distribution of

mineral matter in the peat. In the early stages of peatland development (ie. minerotrophic conditions), dissolved and suspended mineral matter are in abundant supply. Primitive peat-forming plants rooted in mineral sediments are well supplied with nutrients. Since the plants are well fed, and detrital material abundant, these peats are rich in mineral matter. As peat accumulates, successive generations of plants have reduced accessibility to the mineral soil, thus nutrients become less available. In addition, as the peat thickness increases, the amount of dissolved and suspended material carried to the mire will decrease. As a consequence, the amount of mineral matter in the peat decreases over time. When the influence of local groundwaters ceases and the bog becomes ombrotrophic, the Sphagnum mosses depend entirely on precipitation, dry deposition, and their recycling abilities, to sustain themselves. For some elements, notably K, the mosses are very efficient recyclers; below the living (moss) surface K is leached readily.

Ash, Aluminum and Silicon

Reports of detailed investigations of the mineral matter in peats are contained in the proceedings of a recent symposium on the subject, edited by Raymond and Andrejko (1983).

Seven sources of particulates to bog surfaces have been identified: biogenic (e.g. pollen), pedogenic (e.g. soil dust), oceanogenic (near marine systems), pyrogenic (particulates from smoke), plutogenic (from volcanic emanations), cosmogenic (meteoritic dust), and industrial pollutants (Mattson and Koutler-Andersson, 1955). These same authors determined the ash content and total Al and Si through an ombrotrophic bog profile (350 cm deep) at 10 cm intervals. Calculations of the correlation coefficients by this writer gives: for ash and Si, r = 0.892, and for ash and Al, r = 0.899 (n=35).

Silica in peats can be either authigenic (ie. soluble, biogenic silica from plants), or allogenic (ie. insoluble quartz and other silicates, and aluminosilicates). In Sphagnum peats from some Maine bogs 6-10% of the total ash was shown to be soluble silica, and 20-45% was insoluble (Feustel and Byers, 1930). In fens there is more Si available to plants than in bogs and plants that can accumulate Si show this: as much as two-thirds of the ash of Schoenus ferrugineus growing in Swedish fens was found to be SiO_2 (Malmer and Sjors, 1955).

Surface peats are almost always enriched in total ash, but biogenic (soluble) SiO_2 shows no surface enrichment (Feustel and Byers 1930, Chapman 1964). Thus the surface ash enrichment in peats is due to dust, mainly derived from soils. This was shown conclusively by analyzing Sphagnum fuscum, the dominant hummock-forming Sphagnum species (Gorham and Tilton, 1978). The ash contents ranged from 1.6% (in a wilderness area of NW Saskatchewan) to 5.5% (in predominantly agricultural areas of Wisconsin). The ash contents varied directly with the degree of agricultural activity in the areas investigated, demonstrating the pedogenic source of the dust.

Geological controls on ash composition of peats were demonstrated by Salmi (1963). In the granitic terrains of Finland, Sphagnum-dominated peats prevail: here, Al+Si account for 60-70% of the ash. In limestone terrains Salmi found Carex-dominated peats in which Al+Si accounted for only 5-10% of the ash.

Major elements

Studies of Na, K, Mg and Ca in mosses and peat profiles pervade the ecological literature on peatlands. Surprisingly however, there are very few studies of the individual elements per se. Only a few brief remarks on their distribution are made here.

Sodium and Potassium

With all due respect to atomic number 11, the geochemistry of Na in peats is rather unexciting. Sodium is readily leached from peat profiles, and is probably the metallic element "most rapidly and completely removed" from the bog (Damman, 1978).

To show the effect of sea spray on the Na content of peats, a maritime and continental ombrotrophic Sphagnum bog have been compared (Shotyk and Glooschenko, in prep.) In the Barrington bog on the east coast of Nova Scotia the mean Na content of the peat is 352 ppm (n=28); in the Luther bog in southern Ontario the mean Na content is 101 ppm (n=19).

Potassium is highly concentrated by peat-forming plants. For example, in the Okefenokee swamp (Georgia) the surface waters contain approximately 0.5 ppm K and the dry matter of the leaves of Orontium growing there contain 30,000 ppm K (Casagrande and Erchull, 1977). Living Sphagnum mosses are also highly enriched in K relative to subsurface peats. For a Swedish ombrotrophic bog it was calculated that approximately 10% of the total amount of K in the top 4 m

of peat is contained in the upper 5 cm of the profile (Damman, 1978). Below the living moss layer K is readily leached from the peat profile; this explains why organic agricultural soils invariably are K-deficient.

In maritime and continental bogs there is virtually no difference in the K content of the peats: Barrington bog, N.S., mean 206 ppm K (n=28); Luther bog, Ont., mean 226 ppm (n=19) (Shotyk and Glooschenko, in prep.). However, there is a significant difference in the extent of the K enrichment at the surface: Barrington bog, N.S., 0-10 cm 1626 ppm, 10-20 cm 138 ppm, 20-30 cm 105 ppm; Luther bog, Ont., 0-10 cm 439 ppm, 10-20 cm 267 ppm, 20-30 cm 117 ppm. The ratio of the surface K concentrations (1626 ppm K for Barrington/439 ppm K for Luther=3.7) closely corresponds to the large difference in Na inputs (353 ppm Na/101 ppm Na = 3.5), suggesting that plants growing on the maritime bog surface may take up more K to offset the greater atmospheric Na inputs.

Magnesium and Calcium

In seawater the ratio Ca/Mg is approximately 0.3 and in river water approximately 3.0 (weight basis). This difference has enabled investigators to use Ca/Mg ratios in peats as indicators of mire trophy status: peats with Ca/Mg ratios <1 suggest ombrotrophic conditions and Ca/Mg ratios >1 indicate minerotrophic conditions (Mattson, Sandberg and Terning, 1944).

The marine influence on Mg in peats is considerable. The mean Mg content of peats from Barrington bog, N.S. is 1,496 ppm (n=28) and from Luther bog, Ont. 477 ppm (n=19) (Shotyk and Glooschenko, in prep.)

The geological influence on Ca in peats is also striking. In granitic terrains Salmi (1963) found that Ca was <20% of the peat ash, whereas it constituted 40-50% of the ash in limestone terrains. The Barrington bog, N.S. is formed on a granitic basement whereas the Luther bog, Ont., is underlain by calcareous sediments. The mean Ca contents of the peats are 736 ppm (n=28) and 5,795 ppm (n=19), respectively (Shotyk and Glooschenko, in prep.).

Trace elements

The distribution of ash, Cr, Cu, Fe, Mn, Ni, Pb, U, V, and Zn through the peat profiles of approximately 35 mires from Ontario, New Brunswick and Nova Scotia is the subject of a detailed investigation (Shotyk, thesis). Included in the dissertation are all the relevant maps showing the approximate locations of the peatlands investigated, detailed botanical descriptions of the peat profiles, tables of metal analyses, plots of metal concentration vs. ash content and vs. depth, calculations of relative enrichment and depletion of the metals, solubility diagrams for individual elements, etc. Here a few general trends are reported to inspire a general impression of the geochemistry of these metals in peatlands.

For 158 peat samples the following correlation coefficients between metal concentration and ash content have been calculated: Ni 0.839, V 0.786, Cr 0.703, Fe 0.679, Mn 0.568, Cu 0.540, U 0.470, Zn 0.352, Pb -0.126 (for the purpose of the present discussion the correlation coefficient for Pb and ash can be disregarded because the geochemistry of this metal is masked by anthropogenic influences). Based on these correlation coefficients, and considering the appearance of the vertical metal profiles, the known geochemical behaviour of each element, and previously published studies, the order of decreasing correlation between metal content and ash can be viewed as the order of increasing metal mobility in peatlands. That is, of the metals studied here, Ni is the most immobile and Zn the most mobile:

$$Ni < V < Cr < Fe < Mn < Cu < U < Zn$$

In other words, the amount of Ni, V and Cr in any given peat sample depends primarily on the amount of ash whereas additional factors (pH, Eh, affinity toward organic matter, effect of dissolved sulphide on metal solubility) are needed to explain the concentrations of Cu, U and Zn.

Another generalization can be made by comparing the metal concentration in peats, normalized to 100% ash, with the abundance of the metal in typical crustal rocks (Table 4). Factors <2x are considered insignificant. From this comparison it appears that Ni, V, and Cr are neither enriched nor depleted in peats, relative to the composition of typical crustal rocks. This is in agreement with the relative mobilities outlined above.

Copper, Zn, U, and Pb are enriched in the peats by factors of 2x, 2x, 4x and 9x, respectively. The Pb enrichment is almost completely due to atmospheric Pb deposition. The Cu, Zn and U enrichments are reasonable in light of the affinity of organic matter for these elements, the effect of low redox potentials (Cu, U), and the effect of dissolved sulphide (Cu, Zn) on metal solubility. Thus peatlands are geochemical sinks for these 3 metals, and this is well known to exploration

geochemists (see discussion below).

	all peat samples (n=158)	normalized to 100% ash	typical crustal abundance*	enrichment (+) depletion (-)
Ash (%)	9.59	100		
Cr(ppm)	6.2	65	100	-
Cu(ppm)	11.2	118	50	+2
Fe(ppm)	2731	28664	54000	-2
Mn(ppm)	65.7	679	1000	-2
Ni(ppm)	6.2	65	75	-
Pb(ppm)	11.2	117	13	+9
U(ppm)	1.04	11	2.7	+4
V(ppm)	7.7	81	110	-
Zn(ppm)	14.6	151	70	+2

*from Krauskopf (1979)

Table 4 Enrichment/depletion of metals in peats relative to typical crustal rocks

Iron and Mn are depleted from peats, by factors of approximately 2x. This observation previously has been described by the late V.M. Goldschmidt (1954) and is due to the greatly enhanced solubility of Fe and Mn under "reducing" conditions.

The geochemistry of these metals in peats is discussed in order of their increasing mobility in mires.

Nickel

Anthropogenic sources of Ni to the global atmosphere are unimportant relative to the natural fluxes (Table 1). Since Ni is not an essential element for plant growth, surface Ni enrichments in peats should correspond with ash content. An obvious exception would be mires downwind from Ni refineries. In Norway, no regional differences in atmospheric deposition on bog surfaces have been observed (Hvatum et al, 1983), suggesting that anthropogenic sources of Ni are relatively unimportant.

Compounds of Ni are very insoluble and since Ni has no redox chemistry it is expected to exhibit conservative behaviour in peatlands. Mafic rocks such as basalts contain much more Ni than felsic rocks such as granites (150 ppm vs 1 ppm, see Table 2). Soviet workers have shown that Ni in minerotrophic peats developed in mafic terrains contain more Ni than those in felsic terrains (Largin et al, 1972).

Vanadium

Anthropogenic sources of this metal to the global atmosphere are relatively unimportant (Table 1). As in the case of Ni, V is not essential to growing plants so that V surface enrichments in mosses and surface peats should correspond with ash content. In northern Norway bog mosses have slightly less V than in southern Norway, but this may be due to local sources (Rambaek and Steinnes, 1980). In Sphagnum fuscum V decreases from a mean content of 4 ppm in southern Finland to 1 ppm in northern Finland (Pakarinen et al, 1983). Unfortunately Pakarinen and co-workers do not report the ash contents of their samples so that the differences observed may not be out of proportion with ash. Their results may be attributable to increased dry decomposition in the southern part of the country, due to increased agricultural activity.

Like Ni, V forms insoluble compounds and is expected to behave conservatively in peatlands. Vanadium has a limited redox chemistry in natural waters, but forms insoluble hydroxides even at low pH values. Vanadium too, is more abundant in minerotrohic peats formed in mafic vs. felsic terrains. As much as 2% V in peat ash has been reported for a Finnish mire (Salmi, 1955). However, these minerotrophic peats had high ash contents and formed in the vicinity of V-bearing iron ores. In other words, the peats were "contaminated" by V-rich mineral matter, rather than the peats themselves being enriched.

Chromium

Once again, anthropogenic sources of this element to the global atmosphere are relatively unimportant (Table 1). Since Cr is not needed for plant growth, surface Cr enrichments in peats should correspond with ash. In Sweden there are some areas in which mosses contain elevated levels of Cr, however these enrichments are due to local metal industries. In a study of 20 ombrotrophic bogs from across Norway, no significant north-south differences were observed (Hvatum et al, 1983).

Recent studies by soil scientists have provided evidence that Cr (III) can be oxidized to Cr (VI) in soil environments. Sphagnum mosses are depleted in Cr, by a factor of 4x, relative to the mean composition of Carex peat, both normalized to 100% ash (Shotyk, thesis). This depletion can be attributed to oxidation, since Cr (VI) is much more soluble than Cr(III):

$$Cr_2O_3(s)+2H_2O+3/2O_2(g) \rightarrow 2HCrO_4^-+2H^+$$

The oxygen partial pressure (Po_2) for this reaction at equilibrium is approximately 10^{-15} atm. Thus the surface Cr depletion provides useful information about oxidation-reduction conditions at the mire surface. The anion $HCrO_4^-$ can be leached down through

the bog until it encounters conditions more reducing than $P_{O_2} = 10^{-15}$ atm, then precipitate as $Cr_2O_3(s)$ or $FeCr_2O_4(s)$ etc.

Reduction of Cr(VI) in groundwaters to Cr(III) in peats may result in Cr accumulation. In a minerotrophic peatland near Vihanti, Finland, one peat ash sample contained 3000 ppm Cr (Salmi, 1956). The ash content of this well-decomposed (H7) woody Carex peat was only 5%, suggesting that the Cr was enriched in the peat out of proportion with ash. In peat samples from the Sackville copper swamp I have calculated an enrichment factor of approximately 10x for Cr, relative to "normal" peat. Clearly, in areas with bedrock Cr mineralization, Cr enrichments in minerotrophic peats are possible.

Iron

The anthropogenic flux of Fe to the global atmosphere is unimportant relative to the natural flux (Table 1). In surface peats of Norwegian ombrotrophic bogs, no significant differences in Fe content were observed between the northern and southern parts of the country (Hvatum et al, 1983). The metal is essential for plant growth and is quite insoluble under aerobic conditions. Surface Fe enrichments in mires due to enrichments in mineral matter (dust) are probably much greater than contributions from plant concentration and chemical oxidation.

Goldschmidt outlined the two rules which govern the geochemistry of Fe in the weathering cycle:

1) oxidizing conditions promote the precipitation of Fe, reducing conditions promote its solution
2) acid conditions promote the solution of Fe, alkaline conditions promote its precipitation.

It was well known to Goldschmidt that because of the reducing conditions which prevailed throughout their formation, organic agricultural soils were commonly Fe-deficient.

The presence of Fe sulphides such as pyrite, FeS_2, in peats was already well known at the time of Rennie (1810). These sulphides have long been of interest to soil scientists and agriculturalists because their oxidation products are toxic to plants. Except for minerotrophic peats in areas of bedrock-hosted sulphide mineralization or gypsum-bearing sedimentary rocks, peatland waters contain relatively low concentrations of dissolved inorganic sulphur. As a consequence, in most freshwater peats pyritic sulphur is of minor importance relative to organic-S and sulphate-S. It has been suggested that the pyrites which do form in freshwater peats form from the reduction of organic oxysulphur compounds during dissimilatory respiration, generating HS^- or organic sulphides (Altschuler et al, 1983).

The occurrence of vivianite, $Fe_3PO_4 \cdot 8H_2O$ in peats is also well documented (Puustjarvi, 1952; Postma, 1977). In the Vihanti area of Finland bedrock-hosted apatite (Ca phosphate) mineralization at the Vihanti mine generates phosphate-rich groundwaters. In the local eutrophic mires, vivianite is a common occurrence in the peats.

Siderite, $FeCO_3$, is another common Fe-bearing mineral found in minerotrohpic peats. In an exceptional Norwegian peatland some peat samples contain as much as 40% Fe (dry weight basis), mainly due to the occurrence of siderite (Selmer-Olsen and Lie, 1983).

In rich fens in the northern part of central Finland "oily" films floating on the surface of mire surface waters are frequently observed. These iridescent films sometimes are so thick that the water surface looks like a silvered mirror, providing perfect reflections of Menyanthes trifoliata, Equisetum and Carex (personal observation). The films are characteristic of chalybeate (Fe-impregnated or Fe-rich) waters that come into contact with air (Robinson, 1930; Pearsall and Mortimer, 1939; Puustjarvi, 1952). A simplified explanation can be illustrated as

$$Fe(HCO_3)_2^{\circ} + \tfrac{1}{4}H_2O + \tfrac{1}{4}O_2(g) \rightarrow Fe(OH)_3(s) + 2CO_2(g)$$

In minerotrophic (pH>6), CO_2-rich mire waters, much of the dissolved Fe may be complexed with bicarbonate. Upon exposure to the atmosphere the Fe will be oxidized from Fe(II) to the much less soluble Fe(III), and CO_2 will degas, leaving Fe to precipitate as the hydroxide. It is important to stress that the mechanism proposed above is an oversimplification of a complex phenomenon. Puustjarvi has analyzed these "oily" films and found 3-8% Ca, 6-12% Fe and 70-75% organic matter (Puustjarvi, 1952).

Manganese

Like Fe, anthropogenic sources of Mn to the global atmosphere are relatively unimportant (Table 1). In their study of Norwegian ombrotrophic peat bogs, Hvatum et al (1983) found no differences in Mn content from southern to northern Norway.

As with Fe, Mn is essential to growing plants and is much less soluble under aerobic conditions. Surface Mn enrichments are thus the result of plant concentration and Mn oxidation, from Mn(II) to Mn(IV). Manganese enrichment

in surface peats was probably first reported by Feustel and Byers (1930). To illustrate the extent of Mn enrichment, consider these data from Luther bog, Ont. and Barrington bog, N.S.: Luther 0-10cm 39.6 ppm, 10-20cm 7.0 ppm, 20-30 cm 4.0 ppm; Barrington 0-10 cm 84.6 ppm, 10-20 cm 4.0 ppm, 20-30 cm 2.0 ppm (Shotyk and Glooschenko, in prep.).

The two rules governing the behaviour of Fe during the weathering cycle also apply to Mn. Manganese is most mobile under anaerobic and low pH conditions, and most immobile under aerobic and high pH conditions. In peatlands, Mn is expected to be depleted in a way similar to that of Fe. In the Ramna bog in Sweden Fe and Mn both increase with depth through the peat profile, independent of ash content, suggesting a downward leaching of Fe and Mn (Mattson and Koutler-Andersson, 1955).

Copper

The anthropogenic flux of Cu to the global atmosphere exceeds the natural flux by approximately 13 times (Table 1). Using the forest moss Hylocomium splendens a distinct north-south Cu gradient has been demonstrated in Scandinavia; in the south the mosses contain approximately twice as much Cu as they do in remote northern areas (Ruhling and Tyler, 1973) [Note: anthopogenic sources of metals to the atmosphere have declined since the early 1970's See, for example, Ruhling and Tyler (1984)].

In addition to anthropogenic supply and dust, Cu is essential to growing plants. Copper enrichment in surface peats is therefore the result of several factors.

The geochemistry of Cu is characterized by its strongly chalcophile character. It forms very insoluble sulphides and has a tremendous affinity for organic materials. Peatlands are ideal environments for "geochemical trapping" of Cu from natural waters. Lumps of native Cu (ie. metallic copper) as large as an inch in diameter have been found in several peat-forming environments in Montana (Lovering, 1927; Forrester, 1942).

Probably the best studied Cu swamp is the Tantramar swamp near Sackville, New Brunswick. On a dry weight basis some of the peat samples contain as much as 10% Cu and it has been estimated that 300 tons of Cu is contained in the swamp (Boyle, 1977). The waters entering the swamp contain as much as 1 mg l^{-1} Cu; "normal" streams contain approximately 0.005 mg l^{-1} (Drever, 1982). The distribution of Cu in the peat clearly reflects the drainage of water into the deposit: the highest metal concentrations are found in isolated "pockets" surrounding individual seepages of water. These peats contain no more than 0.2% S, thus sulphides cannot be an important metal phase in the peat. No native Cu has been found in these peats. In earlier studies Cu could not be separated from the peat by either "gold panning", heavy bromoform liquid settling, or using an isodynamic separator (Fraser 1961a,b). X-ray diffraction studies have revealed no Cu minerals. The peat is thought to retain the Cu as a metal-organic complex.

A cupriferous swamp in British Columbia has also been studied in detail (Lett, 1978; Lett and Fletcher, 1980). Once again, local groundwaters contain as much as 1 ppm Cu. As a result, the peats in this swamp contain as much as 1% Cu on a dry weight basis. Here, copper sulphide minerals have been identified using SEM: chalcopyrite, $CuFeS_2$, was found as coatings on pyrite framboids, and covellite, CuS, was identified in the interstices between framboids. In addition to these sulphide minerals, grains of native Cu were also observed.

Uranium

Compounds of U(VI) are much more soluble than those of U(IV), thus the migration and distribution of U during the weathering cycle is intimately associated with oxidation-reduction processes (Goldschmidt, 1954). Considering the immobility of U(IV), and the affinity of of U for organic matter, peatlands are as likely to accumulate U as they are Cu.

A classic example of a uraniferous peatland is the one found near Masugnsbyn, Sweden. On a dry weight basis these peats contain as much as 3% U (approximately 10^7 times the abundance of U in typical crustal rocks!). Spring waters in the area had mean background concentrations of 6 $\mu g\ l^{-1}$ U; waters emanating from fracture zones of the bedrock yielded as much as 1800 $\mu g\ l^{-1}$ U (Armands, 1967).

Soviet workers have shown that simple adsorption of U by organic matter would explain enrichment factors as great as 10^4 (Kochenov et al, 1965). Enrichment factors (U concentration in peat/U concentration in water) in uraniferous mires are commonly on the order of 10^6, suggesting some other active enrichment mechanism, in addition to simple adsorption. This mechanism is chemical reduction of U from U(VI) to U(IV):

$$UO_2^{2+} + H_2O \rightarrow UO_2(s) + 2H^+ + \tfrac{1}{2}O_2(g)$$

Sphagnum mosses are depleted in U by

a factor of approximately 8x, relative to the mean composition of Carex peat, both normalized to 100% ash (Shotyk, thesis). This depletion can be attributed to oxidation, since U(VI) is much more soluble than U(IV).:

$UO_2(s) + 2H^+ + \frac{1}{2}O_2(g) \rightarrow UO_2^{2+} + H_2O$

The oxygen partial pressure calculated for this reaction at equilibrium is approximately 10^{-57} atm. The magnitude of the U depletion (8x) is consistent with that of Cr (4x) noted above: at any given Po_2 U will be more strongly depleted than Cr, because U is easier to oxidize. Once again, such metal mobilization can provide some insight into the redox chemistry of the mire.

Once U(IV) is oxidized to UO_2^{2+}, it can be either adsorbed onto the exchange sites on the peat surfaces, or migrate down until it reaches a relatively more reducing microenvironment, at which time it will be reduced back to $UO_2(s)$.

In the Sackville copper swamp I have calculated an enrichment factor of approximately 100x for U, relative to "normal" peat.

Zinc

Anthropogenic sources of Zn to the global atmosphere exceed the natural flux by approximately 23 times (Table 1). In southern Norway surface peats contain more Zn than those in northern Norway (Hvatum et al, 1983). Plant concentration is also important, but may be masked by anthropogenic deposition. Below the living Sphagnum surface Zn is leached quite rapidly: studies in remote northern Norway showed 20 times as much Zn in surface peats (0-10 cm) versus those 50 cm below the bog surface.

An extreme case of Zn enrichment in minerotrophic peatlands is found in Orleans County, New York State. On a dry weight basis some peats there contain as much as 16% Zn (Cannon, 1955). The areas of Zn-rich peat are confined to the lagg zones of the mire, where the peat is in contact with either mineralized zones in the underlying Lockport dolomite or with the highly mineralized groundwater (up to 11 ppm Zn) entering the mire from the sides.

Zinc-rich peats have also been discovered in the Yukon where alkaline (pH 8.1-8.5), sulphate-rich (10-160 mg l^{-1}) waters containing 15-1400 $\mu g\ l^{-1}$ Zn cause the Zn enrichment (Lee et al, 1984). The highest Zn concentration reported was 22% Zn (dry weight basis). The enrichment factors (concentration in bryophyte/concentration in spring water) for Drepanocladus aduncus are Zn 5000, Pb 66 000 and Cd 370,000. The following Zn-bearing minerals were identified in the peat: smithsonite, $ZnCO_3$; wurtzite, ZnS; hemimorphite, $Zn_4Si_2O_7(OH)_2 \cdot H_2O$.

Lead

Anthropogenic fluxes of Pb to the global atmosphere exceed the natural fluxes by approximately 350 times (Table 1). This fact adequately explains surface Pb enrichments in peats. In remote northern Norway, surface peats contain on the order of 2 ppm Pb. In some surface peats of the U.K., Pb concentrations as great as 500 ppm have been reported.

There is no consensus concerning Pb mobility through peat profiles: some workers argue that Pb is mobile, others argue that it is immobile. Considering the low pH of bog surface waters, and the abundance of dissolved organic acids capable of forming extremely stable chelates of Pb, it is difficult to imagine Pb being immobile. However, the question is not so easily answered: dissolved hydrogen sulphide is ubiquitous in mire waters and Pb forms very insoluble sulphides, this certainly would favour immobility. The need for further research of Pb geochemistry in peats is clear.

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